



# THE UNIVERSITY *of* EDINBURGH

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| <b>Title</b>         | Polycyclic dithioles as electron-donors; mechanisms of organic reactions involving elemental sulphur |
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Polycyclic Dithioles as Electron-donors; mechanisms of  
organic reactions involving elemental sulphur.

James Hugh Steven B.Sc.

Doctor of Philosophy  
University of Edinburgh  
1976.



To My Parents

## ACKNOWLEDGEMENTS

I should like to express my thanks to my supervisor Dr. Derek Leaver for his constant advice and suggestions throughout the period of this work; to Dr. E.P. Goodings, my industrial supervisor with whom we had helpful discussions; to Mr. D. Thomas for his tuition and patience in the use of the mass spectrometer; to Mr. J. Grunbaum and also the National Physical Laboratory who carried out elemental microanalysis and finally, to Miss C.E. Wareing for her thoroughness and patience while typing the manuscript.

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During the period of this work I attended a Careers Research and Advisory Council one week course on business appreciation and methods; internal seminars; lecture courses on organometallic chemistry, colloids in industry, industrial management, computer programming, and molecular orbital theory. I also attended two "one day symposia" organised by the Chemical Society and a one day symposium on organic sulphur chemistry organised by Dr. D. Leaver of Edinburgh University Chemistry Department.

In conclusion I should like to express my thanks to all who ~~were~~ involved in organising the above courses and seminars.

*I hereby certify this thesis is entirely my own work and has not been submitted for a degree at any other University*



## Abstract

The synthesis of novel compounds containing two or more 1,2-dithiole rings fused to an aromatic or quinonoid system was undertaken. These syntheses are outlined below:-

- 1) The synthesis of a sulphocarbon based on the mesitylene nucleus was achieved whereas various routes to the sulphocarbon based on the *p*-xylene nucleus proved unsuccessful.
- 2) Routes to naphtho[1,8-cd; 4,5-c'd']bis[1,2]-dithiole and acenaphtho[5,6-cd][1,2]-dithiole were investigated but these syntheses have not been achieved.
- 3) Compounds containing thiathiophthen ring systems fused to anthracene and thiaxanthene nuclei were synthesised and the reaction of anthra(1,9,8-bcde:5,10,4-b'c'd'e')bis(thiathiophthen) with methylating agents studied.
- 4) Routes to the preparation of a compound containing two dithiole rings fused to a pyridazino(4,5-d)pyridazine nucleus were investigated without success.

The cyclo-addition reaction between 1,2-dithiole-3-thiones and arylacetylenes, and the rearrangement of 2-thioacylmethylene-1,3-dithioles to 1,6,6a-trithiapentalenes (6a-thiathiophthens) were further investigated by the following approaches.

- 1) An unambiguous synthesis of the proposed spiran intermediate in the sulphur catalysed rearrangement was attempted but not achieved.
- 2) The effect of vulcanisation accelerators on the rearrangement was studied; the rearrangement appeared to provide a discriminating test of vulcanisation activity.

- 3) The possible intermediacy of thioacylcarbenes in the addition of acetylenes to 1,2-dithiole-3-thiones was investigated; sulphur was shown to participate in the initial formation of adduct.
- 4) The effect of alkyl substituents in the 1,2-dithiole-3-thione on the addition was investigated. The alkyl substituents rendered the 2-thioacylmethylene-1,3-dithiole adduct more labile in its rearrangement to the 1,6,6a-trithiapentalene.

## CONTENTS

### INTRODUCTION

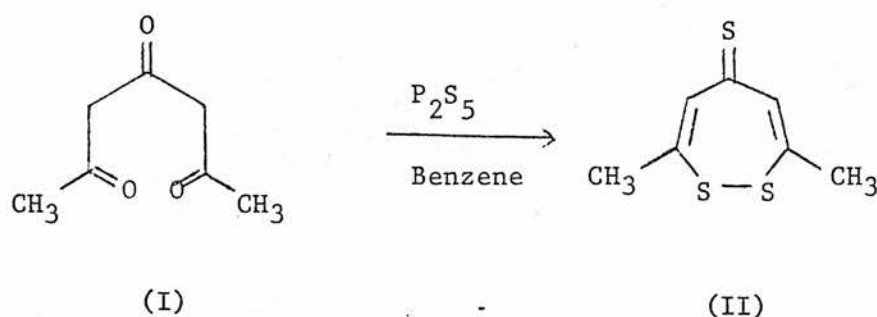
|                   |  |    |
|-------------------|--|----|
| <u>Part A</u>     | 6a-Thiathiophthens   | 1  |
|                   | Formation of Thiathiophthens by Rearrangement of 2-Thioacylmethylene-1,3-dithioles   | 5  |
| <u>Part B</u>     | Compounds Containing 1,2-Dithiole rings fused to Benzenoid and fused Benzenoid systems   | 13 |
| <u>DISCUSSION</u> |  | 30 |
| <u>SECTION 1</u>  | Compounds Containing two or more 1,2-Dithiole rings Fused to a Benzenoid nucleus   | 31 |
| <u>Part (a)</u>   | Preparation of a Sulphocarbon containing the Mesitylene Carbon Skeleton - C <sub>9</sub> S <sub>9</sub>  | 32 |
| <u>Part (b)</u>   | Attempted Preparation of a Sulphocarbon Containing the p-Xylene Carbon Skeleton - C <sub>8</sub> S <sub>8</sub>  | 37 |
| <u>SECTION 2</u>  | Compounds Containing one or more 1,2-Dithiole rings Fused to a Naphthalene Nucleus   | 44 |
| <u>Part (a)</u>   | Attempted Synthesis of Naphtho[1,8-cd; 4,5-c'd']bis[1,2]-dithiole  | 45 |
| <u>Part (b)</u>   | Attempted Synthesis of Acenaphtho[5,6-cd][1,2]-dithiole  | 47 |
| <u>SECTION 3</u>  | Compounds containing Thiathiophthen Ring Systems Fused to an Anthracene or to a Thioxanthene Nucleus   | 51 |
| <u>Part (a)</u>   | Synthesis of Bridged Dibenzothiathiophthens  | 53 |
| <u>Part (b)</u>   | Characterisation and Reactions of Anthra(1,9,8-bcde: 5,10,4-b'c'd'e')bis(thiathiophthen)   | 61 |
| <u>SECTION 4</u>  | Attempted Synthesis of a Polysulphide Containing a Pyridazino(4,5-d)Pyridazine Nucleus   | 73 |
| <u>SECTION 5</u>  | Reaction of Acetylenes with 1,2-Dithiole-3-thiones and the Rearrangement of 2-Thioacylmethylene-1,3-dithioles to 1,6,6a-Trithiapentalenes (6a-Thiathiophthens) | 76 |
| <u>Part (a)</u>   | The Proposed Spiran Intermediate   | 76 |
| <u>Part (b)</u>   | The Effect of Vulcanisation Accelerators on the Sulphur Catalysed Rearrangement  | 79 |

|                     |  |     |
|---------------------|--|-----|
| <u>Part (c)</u>     | The Possible Intermediacy of Thioacylcarbenes<br>in the Reaction of Acetylenes with 1,2-Dithiole-<br>3-thiones   | 80  |
| <u>Part (d)</u>     | The Effect of Alkyl Substituents in the 1,2-Dithiole-<br>3-thione  | 85  |
| <u>EXPERIMENTAL</u> |  | 90  |
| Notes               |  |     |
| <u>SECTION 1</u>    | Preparation of Compounds containing a Benzene Nucleus  | 92  |
| <u>SECTION 2</u>    | Preparation of Compounds containing a Naphthalene<br>Nucleus   | 100 |
|                     | Preparation of Compounds containing an Acenaphthylene<br>Nucleus   | 102 |
| <u>SECTION 3</u>    | Preparation of Compounds containing a Xanthene<br>or Thioxanthene Nucleus  | 108 |
|                     | Preparation of Compounds containing an Anthracene<br>Nucleus   | 117 |
|                     | Reactions of Anthra(1,9,8-bcde:5,10,4-b'c'd'e')  | 123 |
|                     | bis(thiathiophthen)  |     |
| <u>SECTION 4</u>    | Preparation of Compounds containing a<br>pyridazino[4,5-d]pyridazine nucleus   | 127 |
| <u>SECTION 5</u>    | Preparation of Compounds involved in Investigations<br>into the reaction of Acetylenes with 1,2-Dithiole-<br>3-thiones and the Rearrangement of 2-Thioacylmethyl-<br>ene-1,3-dithioles to 1,6,6a-Trithiapentalenes | 132 |
| <u>Part (a)</u>     | Preparation of Compounds involved with the Proposed<br>Spiran Intermediate   | 132 |
| <u>Part (b)</u>     | Experiments to evaluate the effect of<br>Vulcanisation Accelerators  | 137 |
| <u>Part (c)</u>     | Experiments to determine the Possible Intermediacy<br>of Thioacylcarbenes  | 140 |
| <u>Part (d)</u>     | Experiments to Determine the Effect of Alkyl<br>Substituents in the 1,2-Dithiole-3-thione  | 144 |
| U.v. Spectra        |  | 149 |
| References          |  | 152 |

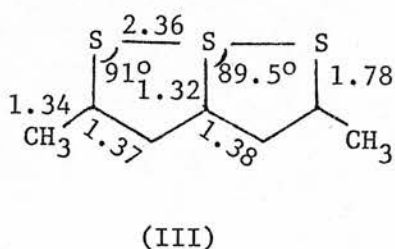
## INTRODUCTION

## Part A. 6a-Thiathiophthens

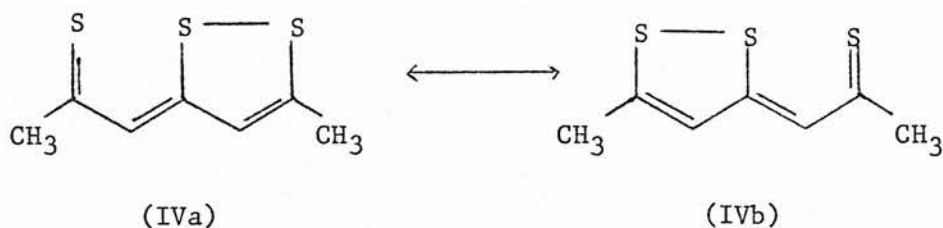
An investigation by Arndt et al,<sup>(1)</sup> in 1925 into the reaction between diacetylacetone (I) and phosphorus pentasulphide, resulted in their obtaining a product to which the structure (II) was assigned on the basis of elemental analysis and molecular weight.



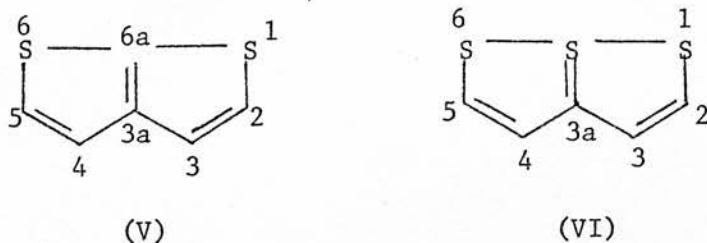
Evidence in contradiction of this structure did not appear until 1958, when an X-ray analysis by Bezzi et al<sup>(2,3,4)</sup> established the structure (III) containing a linear system of three equally spaced sulphur atoms. The S-S bond length ( $2.36\text{\AA}$ ) was considerably shorter than twice the van der Waals radius of sulphur ( $3.70\text{\AA}$ ) but longer than that of the normal disulphide bond ( $2.04\text{\AA}$ ).



This result was explained by postulating resonance between two equivalent structures (IVa, IVb) which exemplify a type of electron delocalisation known as "single bond - no bond resonance".

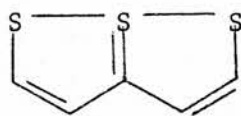


Compounds of this type are formally 3-thioacylmethylene-1,2-dithioles but, because of the analogy with thiophthen (V) when the central sulphur atom is represented as tetravalent, the generic name of 6a-thiathiophthen (VI) has been adopted.

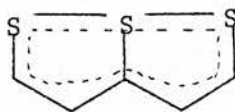


Alternatively, the ring-system of (VI) may be regarded as related to the hydrocarbon pentalene. Thus the name of the parent compound (VI) becomes 1,6,6a-trithiapentalene and compound (III) is 2,5-dimethyl-1,6,6a-trithiapentalene (2,5-dimethyl-6a-thiathiophthen).

Since the work of Bezzi in 1958, many 6a-thiathiophthens have been prepared<sup>(5)</sup> and much controversy has arisen concerning the fine structure of the system. They have been represented as "single bond - no bond" resonance hybrids (IVa, IVb), as structures containing tetravalent sulphur (VII) or as structures containing an "electron-rich 3-centre bond" which is stabilised to some extent by  $\pi$ -electron conjugation (VIII).



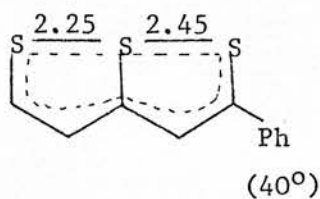
(VII)



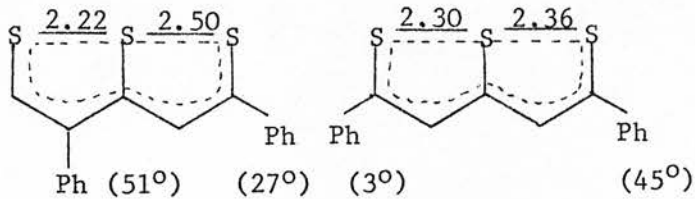
(VIII)

There is now fairly good agreement between experimental and theoretical studies that the best representation of the  $10\pi$ -electron system is given by (VIII)<sup>(6,7)</sup>. Each sulphur atom retains 2 unshared 3 S-electrons, the terminal sulphur atoms contribute 2 electrons to  $\sigma$ -bonds and 2 electrons to  $\pi$ -bonds, and the central sulphur atom contributes 3 electrons to  $\sigma$ -bonds and 1 electron to  $\pi$ -bonds. The  $5\pi$ -electrons from the 5-carbon system combine with the 5  $\pi$ -electrons from the sulphur atoms to form a  $10\pi$ -electron system.

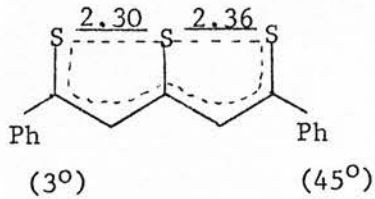
Crystallographic studies<sup>(8)</sup> show that different substituents on 6a-thiathiophthens perturb the fine balance of the three sulphur sequence to different degrees, so that the S-S bond-lengths vary over the range  $2.2 - 2.5\text{\AA}$ .



(IX)<sup>9</sup>

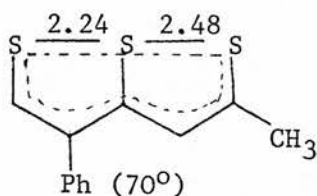


(X)<sup>10</sup>

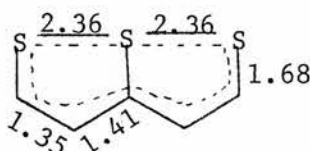


(XI)<sup>11</sup>

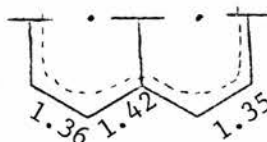




(XII)<sup>12</sup>



(XIII)<sup>8</sup>



(XIV)<sup>13</sup>

The CNDO/2 molecular orbital calculations of Hordvik et al<sup>(14)</sup> agree closely with those of Clark and Kilcast<sup>(15)</sup> which show that the curve representing potential energy as a function of the displacement of the central sulphur atom from its mean position has a flat "minimum" extending over ca, 0.3Å. Gleiter and Hoffmann<sup>(16)</sup> obtained similar results to those of Hordvik by using extended Hückel calculations.

The calculations predict that substitution by a 2-methyl (III) or 2-phenyl (IX, X, XI) group should lengthen the  $S_1 - S_{6a}$  bond length, whereas a 3-methyl or 3-phenyl group should shorten the bond length. The effect of a 2-phenyl group depends on the angle of twist of the connecting bond. A twisted phenyl group is noted to have a greater lengthening effect on the adjacent S-S bond, than a phenyl group which is coplanar with the carbon ring system.

A feature which has emerged from the X-ray work is the similarity in geometry of the 5-carbon chain in 6a-thiathiophthene (XIII) to one half of the naphthalene molecule (XIV)<sup>(13)</sup>.

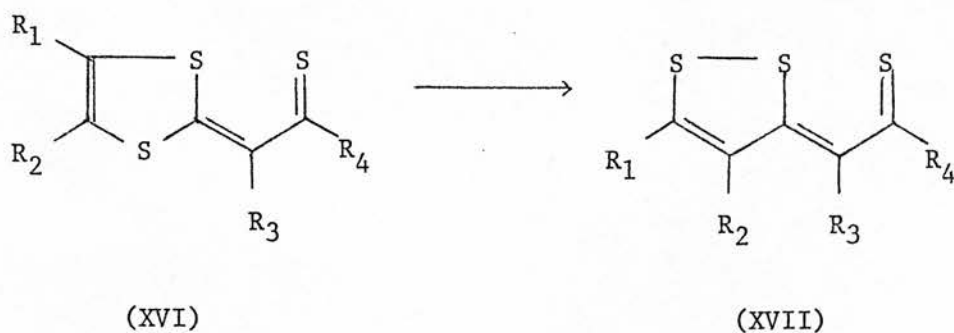
The p.m.r. spectra of 6a-thiathiophthens indicate the symmetry of the system<sup>(5,7,17,18,19,20)</sup> but these cannot distinguish between a time-independent structure such as (IVa)  $\leftrightarrow$  (IVb), (VI) or

(VII) and a rapidly established tautomeric equilibrium (IVa)  $\rightleftharpoons$  (IVb). The spectrum which results could be a time average of the spectra of the tautomeric forms which in effect simulates the symmetry otherwise attributable to resonance.

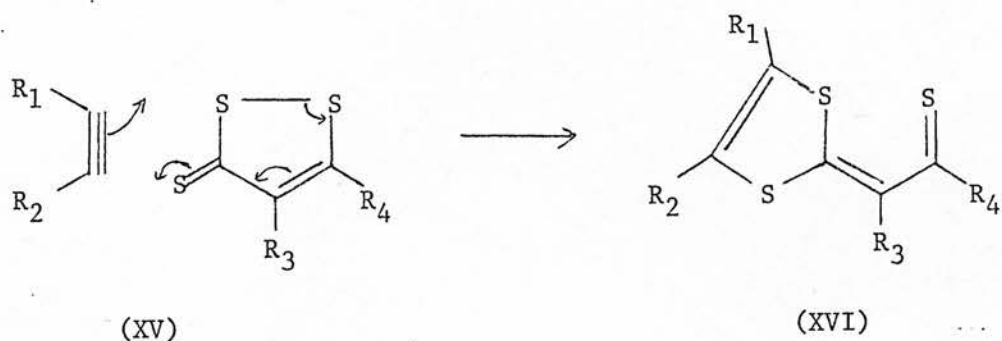
Many studies have been carried out using u.v. spectra of 6a-thiathiophthens<sup>(21)</sup> and their precursors, however they give no specific structural information. The electronic spectrum<sup>(22)</sup> of 2,5-dimethyl-6a-thiathiophthen (III) using polarised light has been interpreted as suggesting an unsymmetrical structure, but measurements by X-ray photoelectron spectroscopy<sup>(15)</sup> of 6a-thiathiophthen (XIII), and 2,5-dimethyl-6a-thiathiophthen (III) indicated only two types of sulphur atom i.e. the 1- and 6-, and 6a-sulphur atoms.

#### Formation of Thiathiophthens by Rearrangement of 2-Thioacylmethylene-1,3-dithioles

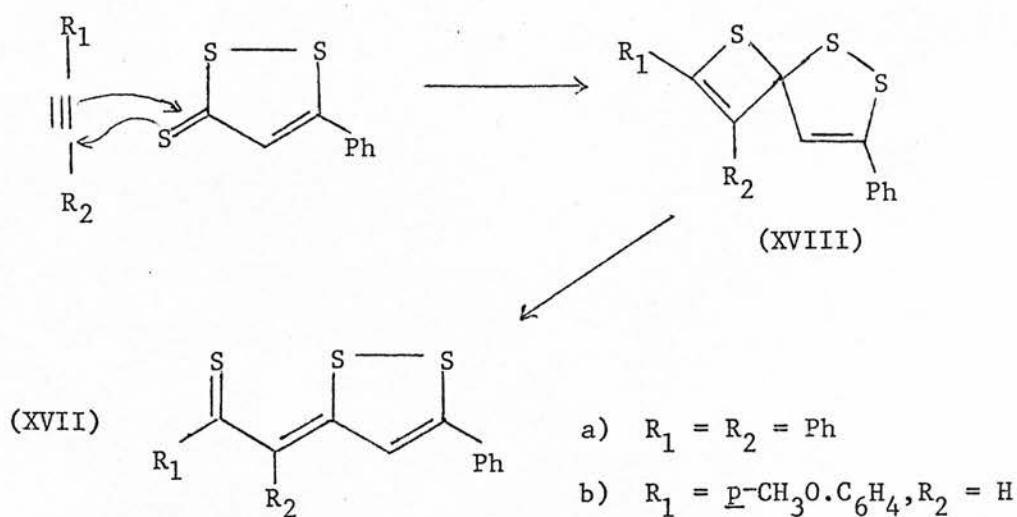
Although 6a-thiathiophthens can be synthesised by a number of methods<sup>(5,23)</sup> the route most pertinent to this thesis is via the rearrangement of the isomeric 2-thioacylmethylene-1,3-dithioles<sup>(24)</sup> (XVI).



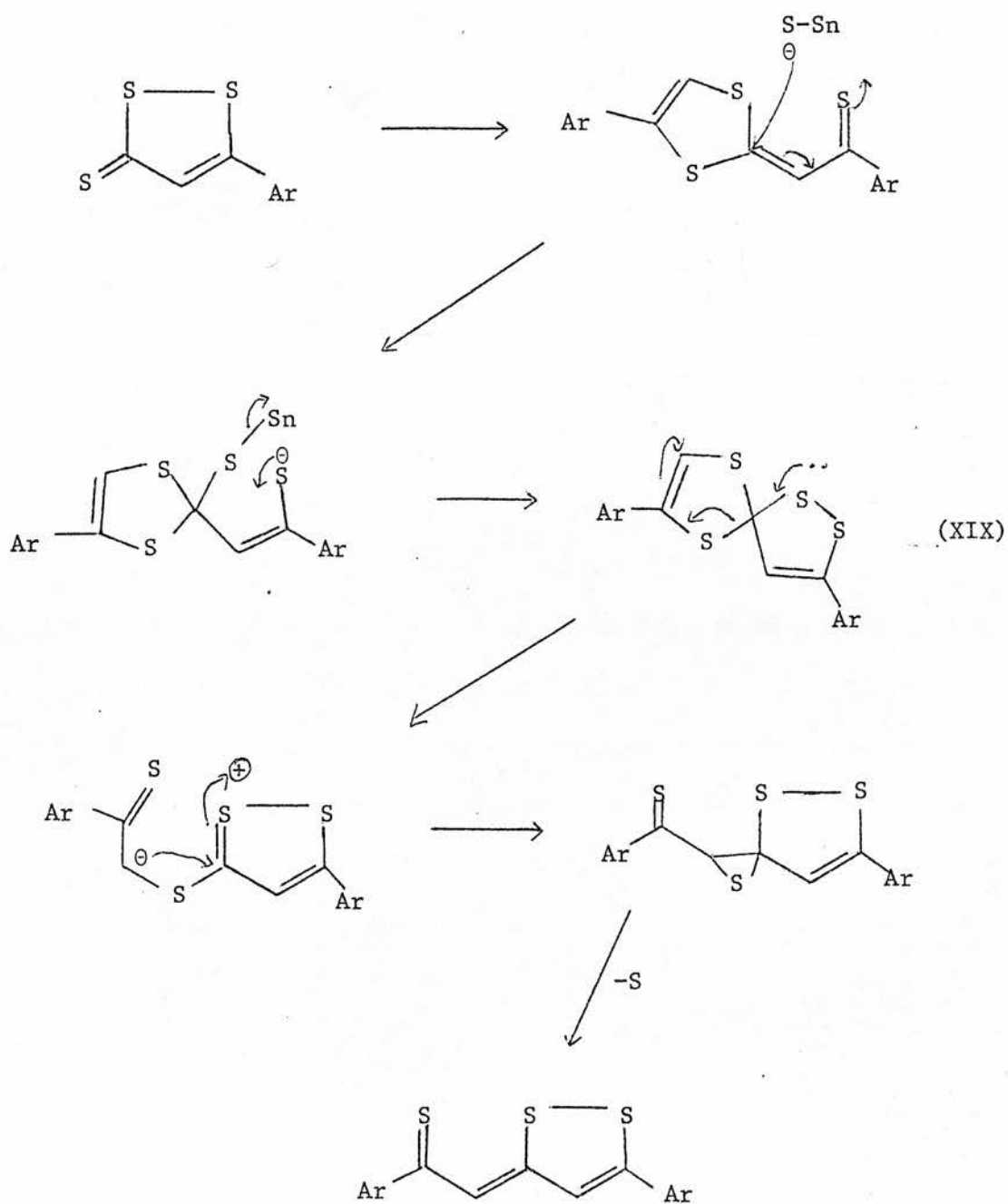
The 2-thioacylmethylene-1,3-dithioles are prepared by a 1,3-cycloaddition of aryl acetylenes to the corresponding 1,2-dithiole-3-thione<sup>(25,26)</sup> but Behringer noted that diphenyl acetylene ( $R_1 = R_2 = \text{Ph}$ ) and *p*-methoxyphenylacetylene ( $R_1 = \text{p-CH}_3\text{OC}_6\text{H}_4$ ,  $R_2 = \text{Ph}$ )



reacted with 5-phenyl-1,2-dithiole-3-thione ( $R_3 = \text{H}$ ,  $R_4 = \text{Ph}$ ) to give the corresponding 6a-thiathiophthen (XVII). It was proposed that the 6a-thiathiophthens were generated via an intermediate (XVIII) produced by 1,2-cycloaddition across the exocyclic  $\text{C} = \text{S}$  bond.



Vialle and co-workers<sup>(24,27)</sup> observed the formation of the adducts (XVI) or thiathiophthens on variation of the reaction



Scheme 1

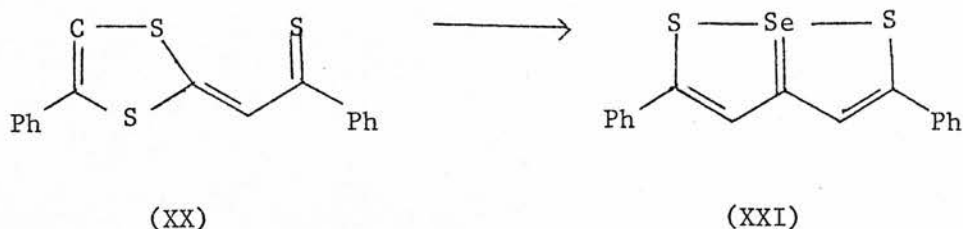
conditions. Like Behringer, they suggested initially that 1,2-cycloaddition was responsible for the formation of 6a-thiathiophthens but in a later report<sup>(28)</sup> stated that 2-thioacylmethylene-1,3-dithioles were always the initial products of the cycloaddition and that subsequent rearrangement to the 6a-thiathiophthen was catalysed by the 1,2-dithiole-3-thione. Phosphorus pentasulphide was found to effect the same transformation.

Investigations<sup>(29,30)</sup> within this department have shown the rearrangement to proceed thermally and elemental sulphur to be a more effective catalyst than the dithiolethione. It was shown, moreover, that rigorously purified dithiolethiones do not yield 6a-thiathiophthens on reaction with acetylenes unless sulphur is added. In the absence of sulphur, 2-thioacylmethylene-1,3-dithioles are formed and it seems unlikely that 1,2-cycloaddition to the C = S group can be responsible for the thiathiophthen formation since this reaction should proceed equally well in the absence of sulphur.

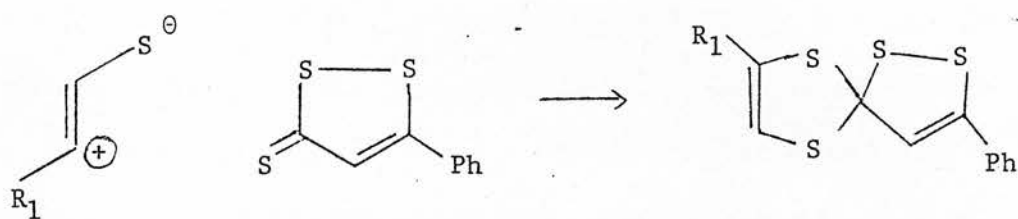
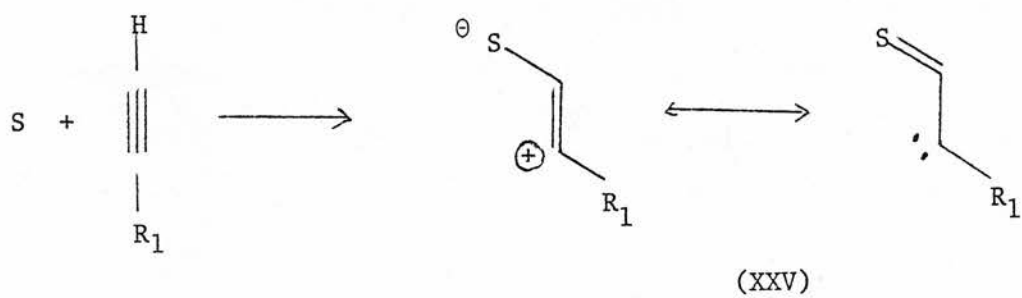
The mechanism proposed by Davidson and Leaver<sup>(29)(30)</sup> for the rearrangement of 2-thioacylmethylene-1,3-dithiole is shown in scheme 1 and involves the participation of a reactive polysulphur species formed either by thermal fission of the S<sub>8</sub> ring or by attack on the S<sub>8</sub> ring by an unrecognised nucleophilic impurity. Nucleophilic attack by this reactive polysulphide at the 2-position of the 1,3-dithiole ring followed by intramolecular nucleophilic displacement at the first atom of the attached polysulphur chain leads to a spiran intermediate (XIX).

A 1,2-dithiolylium cation is then formed by opening of the 1,3-dithiole ring which thus becomes a thioenolate grouping. The remaining stages of episulphide formation and sulphur extrusion to form the 6a-thiathiophthen are analogous to the stages involved in the base-induced conversion of 3-phenacylthio-1,2-dithiolylium salts into 3-phenacylidene-1,2-dithioles<sup>(31,32,33)</sup>.

The suggested mechanism requires that the central sulphur atom of the thiathiophthen is derived from the sulphur catalyst and supporting evidence for it was obtained by boiling the 1,3-dithiole (XX) with selenium in 1,2,4-trichlorobenzene. This generated the 6a-selenathiophthen (XXI) along with an equal amount of 6a-thiathiophthen. When the 6a-thiathiophthen was heated under the same conditions with selenium present, no exchange of sulphur for selenium occurred.



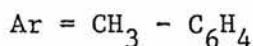
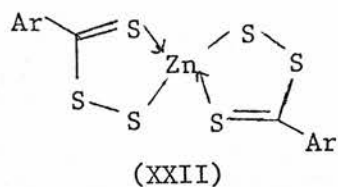
Vulcanisation accelerators (zinc dibenzylldithiocarbamate, 2-mercaptobenzothiazole, tetramethylthiuram disulphide) were shown to accelerate the sulphur-catalysed rearrangement, but in the case of metal-free accelerators little acceleration occurred unless zinc oxide was present. However, zinc oxide alone, was shown to produce little effect on the rearrangement.



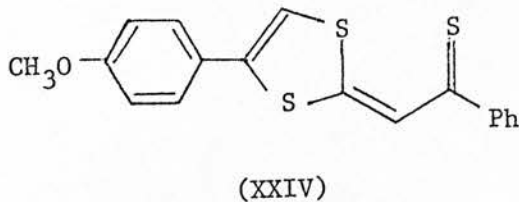
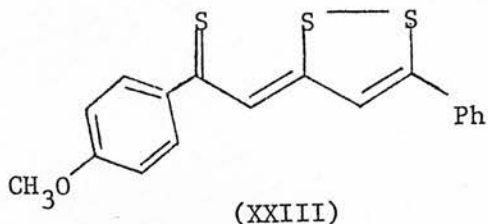
Scheme 2

These results are readily accommodated within the proposed mechanism by taking account of the suggestion of Bateman, Glazebrook and Moore<sup>(34)</sup> that the effect of accelerators in the vulcanisation process depends on their reaction with sulphur to form polysulphur anions ( $R - S_n - S^\ominus$ ).

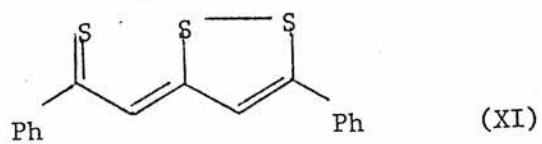
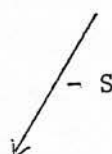
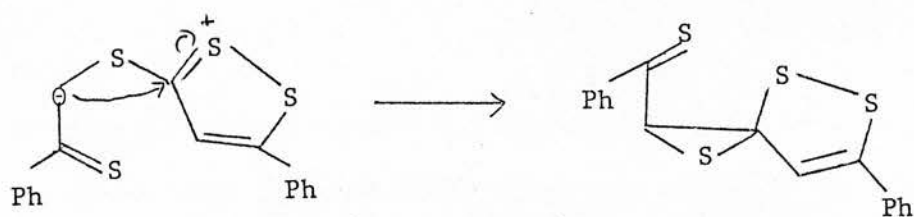
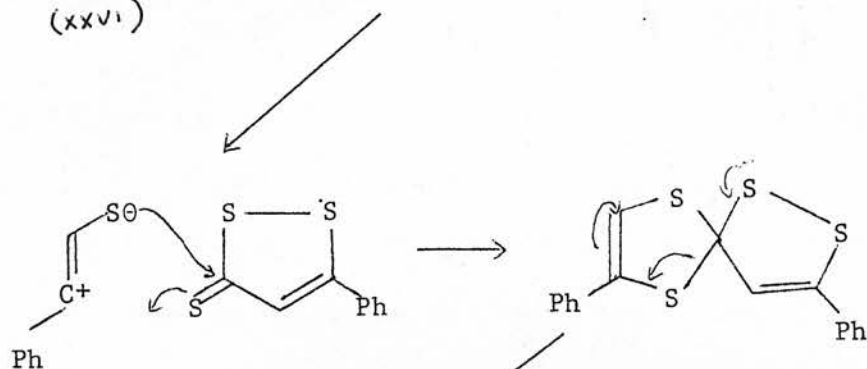
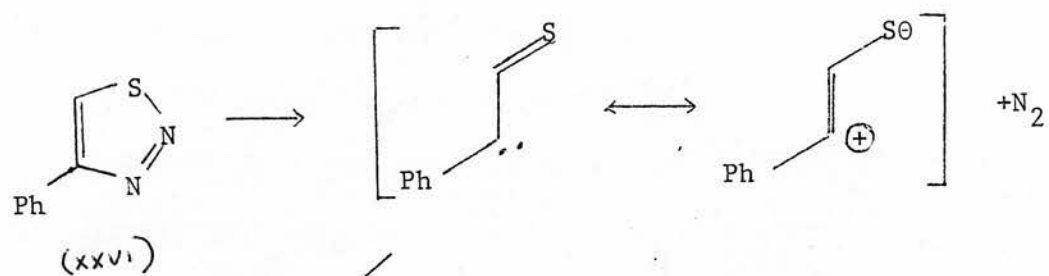
Also in accord with the mechanism was the observation that the sulphur-rich zinc complex (XXII) described by Fackler<sup>(35,36)</sup> and his co-workers acts as a highly effective catalyst for the rearrangement even in the absence of elemental sulphur.



Some of the experiments carried out by Davidson suggested, though the evidence was not entirely convincing, that thiathiophthens (e.g. XXIII) were formed more rapidly by direct reaction of the dithiolethione with the acetylene, in the presence of sulphur, than by the rearrangement of the corresponding 2-thioacylmethylene-1,3-dithiole (XXIV) under comparable conditions.





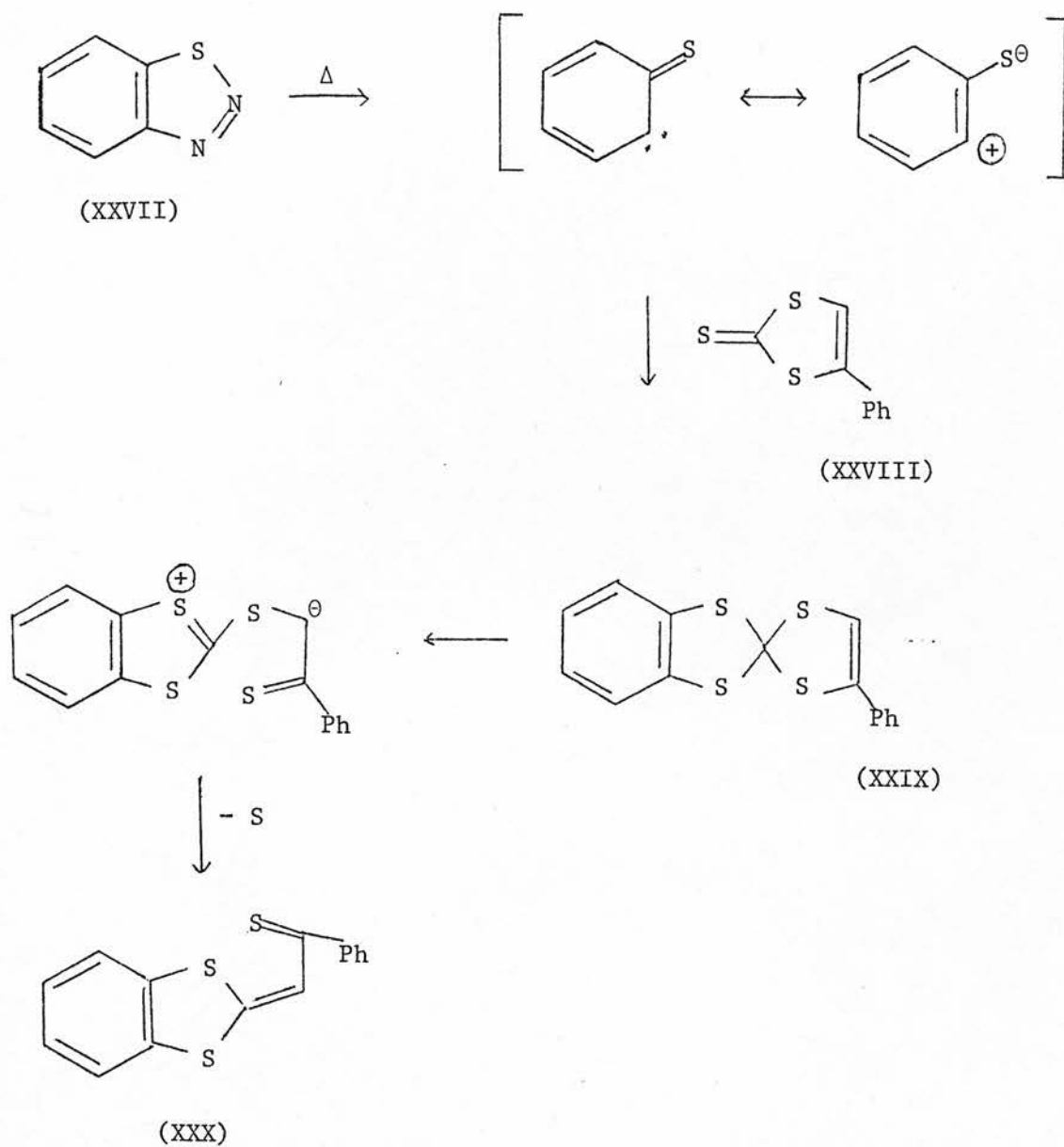


Scheme 3

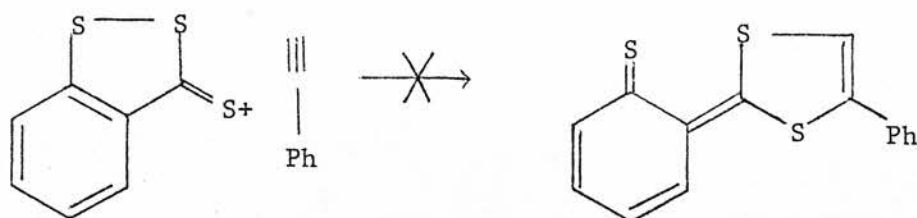
It seemed possible therefore, that there might be an alternative route to the 6a-thiathiophthens involving reaction between the acetylene and sulphur to form a thioacylcarbene (XXV) which could then form the spiran intermediate by 1,3-dipolar cycloaddition to the thiocarbonyl bond of the dithiolethione (Scheme 2).

To test this hypothesis 4-phenyl-1,2,3-thiadiazole (XXVI), which would appear to be a suitable precursor of the thioacylcarbene, was heated with 5-phenyl-1,2-dithiole-3-thione. No reaction occurred in boiling xylene but, at 200°C in the absence of a solvent, 2,5-diphenyl-6a-thiathiophthen (XI) was formed. (Scheme 3).

A number of related reactions in which 4-phenyl- and 4,5-benzo-1,2,3-thiadiazole were thermolysed in the presence of 1,3-dithiole-2-thiones, yielded related products and established the formation of spirodithioles and their mode of decomposition by opening of the 1,3-dithiole ring and loss of sulphur. Of these reactions the one which provided the most convincing evidence for a spiro-intermediate was that of 4,5-benzo-1,2,3-thiadiazole (XXVII) with 4-phenyl-1,3-dithiole-2-thione (XXVIII). The product here was 4,5-benzo-2-thiophenacylidene-1,3-dithiole (XXX) which could only have been produced via the spiro-compound (XXIX) and which was stable to further rearrangement owing to the presence of a fused benzene ring.

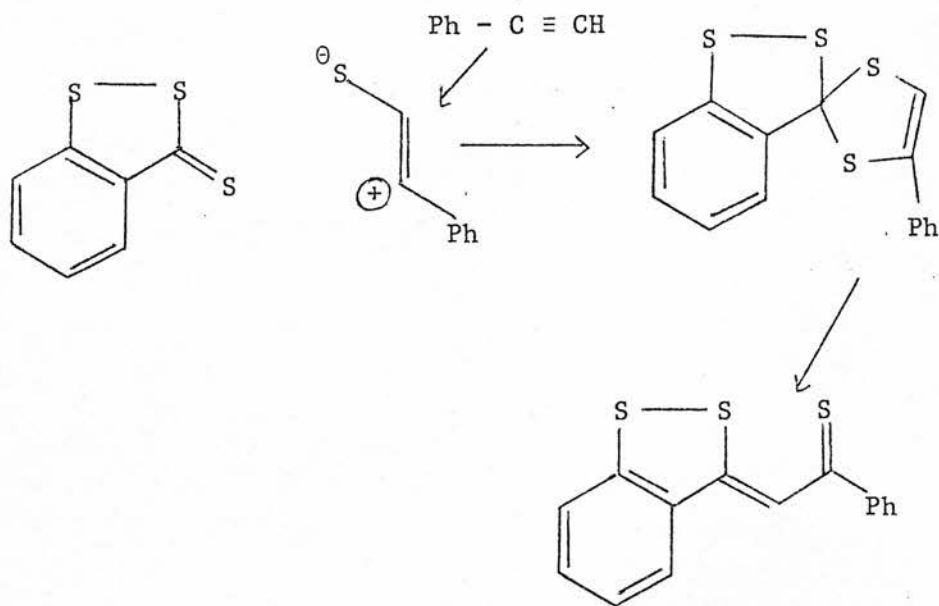


Additional evidence for the direct participation of sulphur in the acetylene-1,2-dithiole-3-thione reaction was provided by studying the reaction of phenylacetylene with 4,5-benzo-1,2-dithiole-3-thione (XXXI). In the absence of sulphur, little reaction occurred and no identifiable product was obtained; this can be attributed to the difficulty of forming an o-quinonoid ring by the usual mode of cycloaddition:-

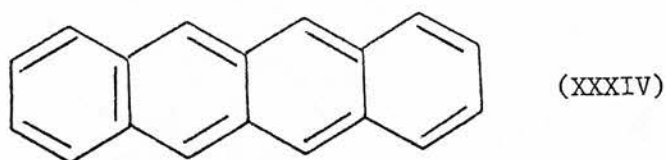


(XXXI)

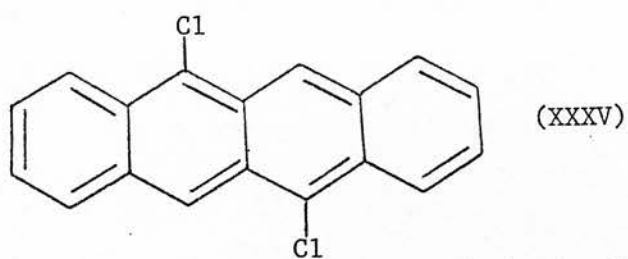
In the presence of sulphur, a small yield of the benzothia-thiophthen (XXXII) was obtained, in accord with a mechanism involving the formation of a thioacylcarbene which then adds to the thiocarbonyl group to form a spirodithiole:-



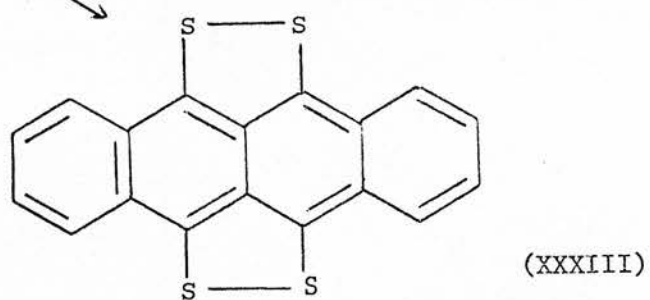
(XXXII)



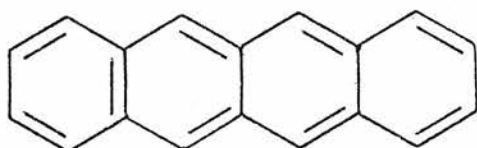
$S_2Cl_2$  (Trichlorobenzene)



$S_2Cl_2$  (Trichlorobenzene)



$S_8$  (Trichlorobenzene)

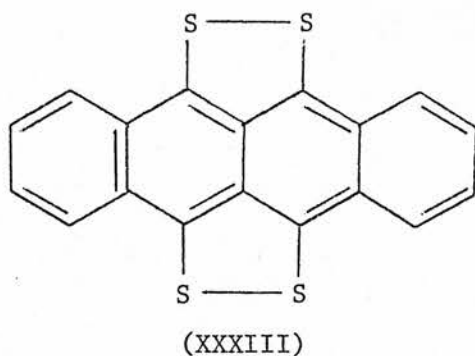


Scheme 4

Part B. Compounds Containing 1,2-dithiole rings fused to  
Benzenoid and Fused Benzenoid Systems

Compounds have been reported which have dithiole groupings fused to acene systems and these have a formal relationship to other dithioles and also to 6a-thiathiophthens.

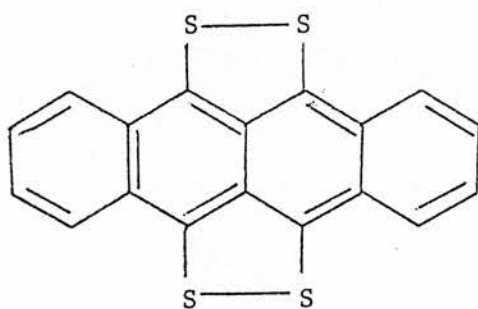
In a series of papers,<sup>(37-41)</sup> Marschalk et. al. described the preparation and properties of the tetracenobis(1,2-dithiole) (XXXIII), often referred to as "tetracene tetrasulphide" (TTS) and tetrathiotetracene (XXXIII).



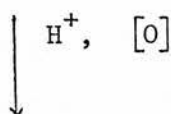
Tetrathiotetracene was obtained by the reaction of tetracene (XXXIV) with elemental sulphur in boiling trichlorobenzene or, more rapidly, by reaction with disulphur dichloride under the same conditions. An intermediate in the latter reaction was shown to be 9,11-dichlorotetracene (XXXV) which in an independent reaction afforded tetrathiotetracene (XXXIII) on further treatment with disulphur dichloride<sup>(29)</sup> (scheme 4).

During Marschalk's structural investigations, 9,10,11,12-tetra(methylthio)- and -tetra(benzylthio)-tetracene (XXXVI, R = Me and R = Ph.CH<sub>2</sub>) were obtained from tetrathiotetracene by reduction with sodium in liquid ammonia followed by reaction with the appropriate chloro-compound.

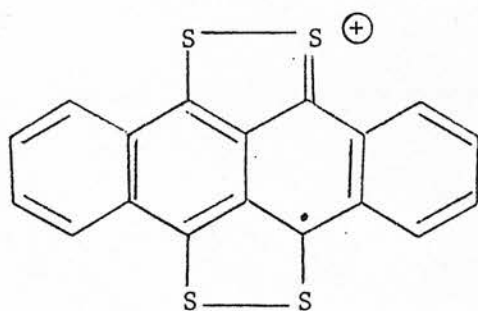
(XXXIII)



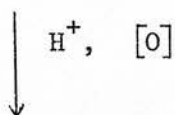
$$(\sigma_{20} = 5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1})$$



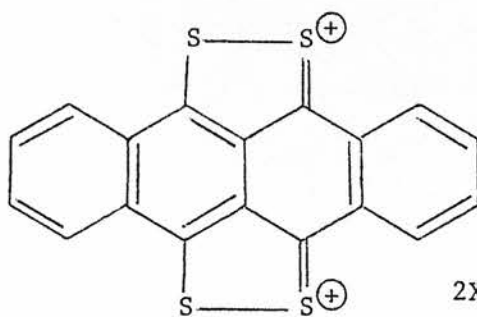
(XXXVIII)



$$\text{X}^{\ominus} (\sigma_{20} = 1 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1})$$



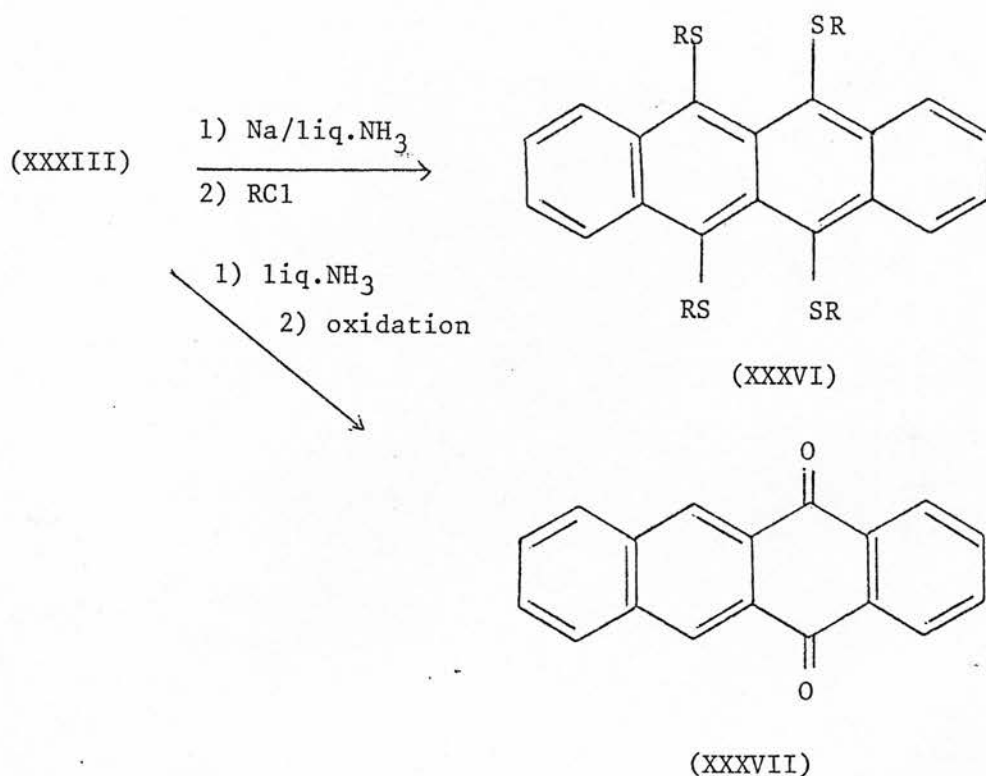
(XXXIX)



$2\text{X}^-$

$$(\sigma_{20} = 3 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1})$$

Scheme 5



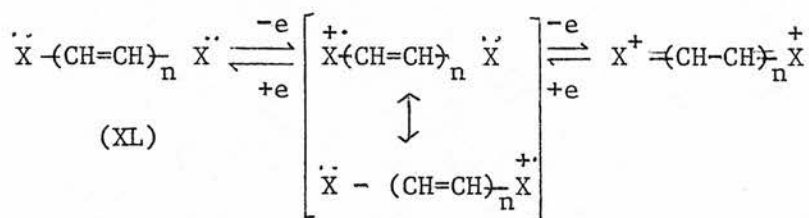
Reaction of the tetrasulphide, in an autoclave, with liquid ammonia, followed by oxidation, yielded tetracene-9,10-quinone (XXXVII).

The radical-cation (XXXVIII) and dication (XXXIX) of tetrathiotetracene are formed by reaction with strong acid in the presence of an oxidising agent or, in the case of the dication, also by direct reaction with halogen (scheme 5). Regeneration of the tetrathiotetracene can be effected using titanium trichloride or sodium dithionite as the reducing agent.

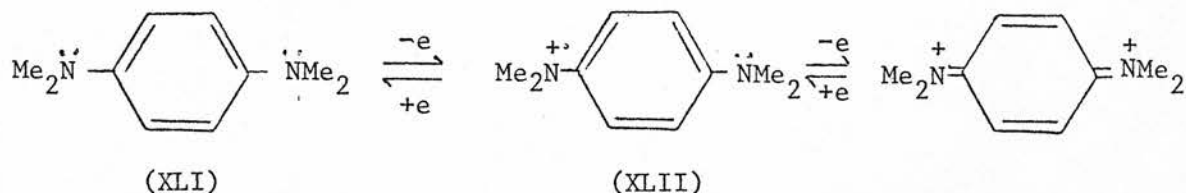
The formation of a stable radical-cation by oxidation of tetrathiotetracene is characteristic of polyenic or aromatic systems (XL) bearing electron-pair donor substituents on the first and 2nth carbon atoms.<sup>(42)</sup> In many such systems there is evidence that further oxidation can lead to a dication, though stable salts of this are not always isolable. The complete series of redox



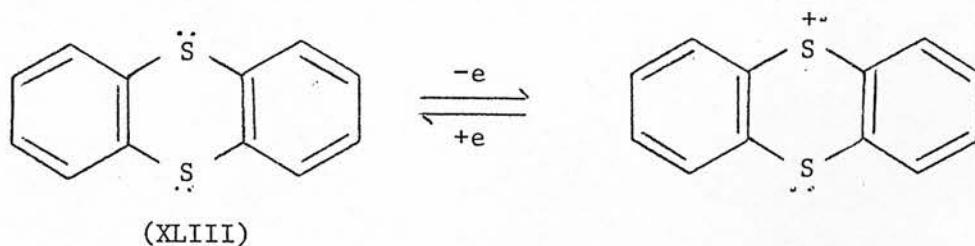
equilibria may be represented by the general scheme



The classical example<sup>(43)</sup> of such an oxidation is the formation of Wursters blue radical cation (XLII) by oxidation of tetramethyl-p-phenylenediamine (XLI) and a typical example<sup>(44)</sup>

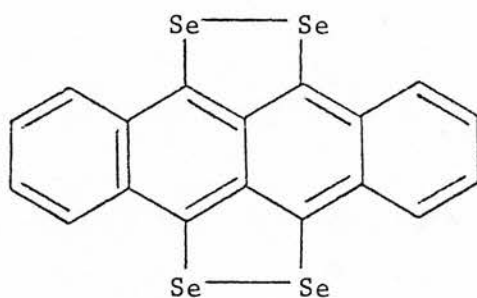


in which sulphur serves as the donor atom is the oxidation of thianthrene (XLIII).



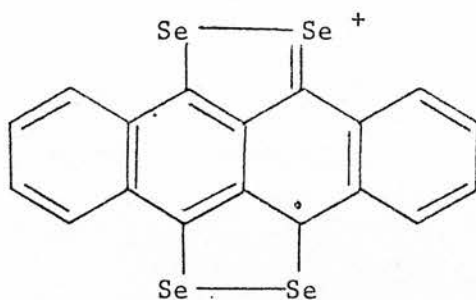
In the case of tetrathiotetracene, the radical-cation may be expected to gain stability owing to the contribution of canonical structures (XLIV a,b) containing a dithiolium nucleus:-

(XLVI)



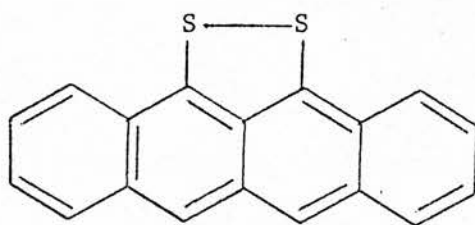
$$(\sigma_{20} = 2 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1})$$

(XLVII)



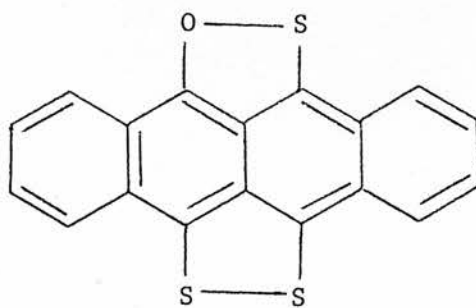
$$(\sigma_{20} = 2 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1})$$

(XLVIII)

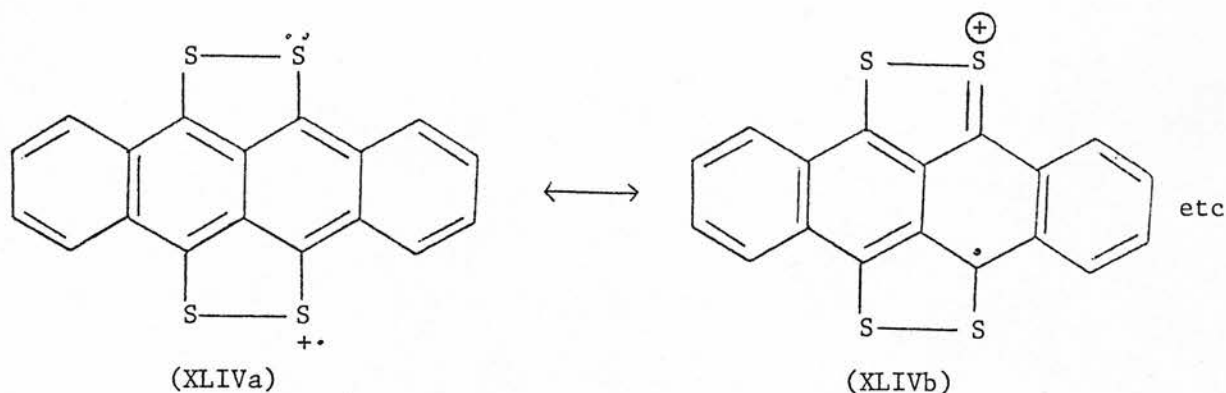


$$(\sigma_{20} = 6 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1})$$

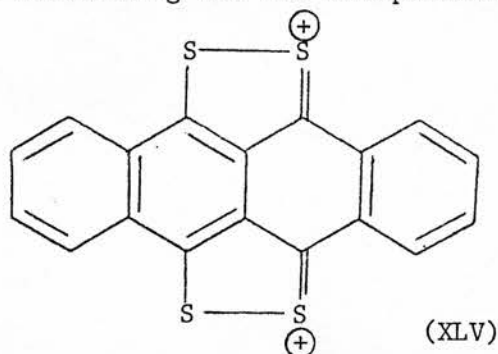
(IL)



$$(\sigma_{20} < 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1})$$

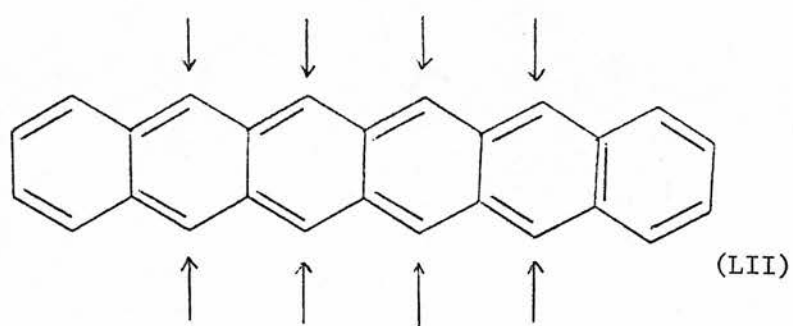


Similarly, the dication may be formulated as a bis dithiolium salt (XLV), thus accounting for its exceptional stability.

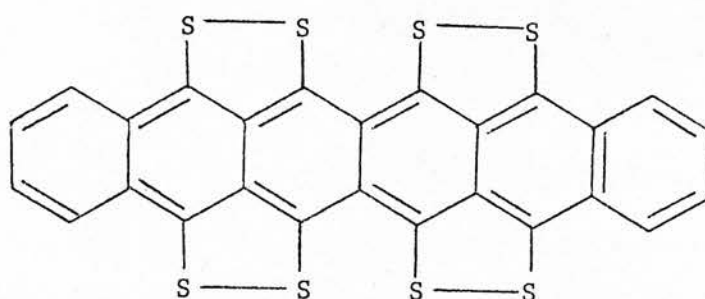


The reaction of selenium with 9,11-dichlorotetracene (XXXV) yielded along with other poorly defined materials, tetraselenotetracene (XLVI) which forms salts analogous to those of tetrathiotetracene (XXXIII)<sup>(45)</sup>.

The molecular structure<sup>(46)</sup> of tetrathiotetracene has now been fully established by X-ray diffraction. Matsunaga<sup>(47)</sup> was the first to report that tetrathiotetracene and its complexes with strong electron acceptors such as o-chloranil, o-bromanil, and tetracyanoethylene, show unusually high electrical conductivities and various aspects of this property such as the dependence on pressure<sup>(48,49)</sup> and temperature<sup>(50)</sup> have been reported. Electrical conductivities have also been reported by Goodings et. al.,<sup>(45)</sup> of ICI Corporate Laboratory, for tetrathiotetracene and related compounds and these values are shown here in parenthesis alongside the relevant formulae. Further work carried out within ICI resulted

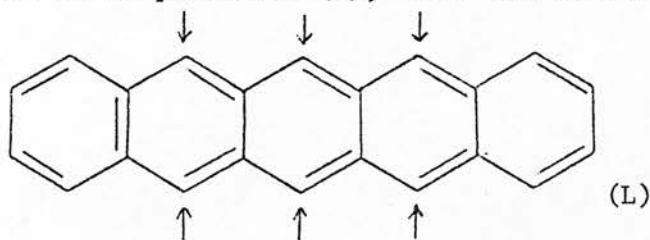


$S_8$ /(Trichlorobenzene)

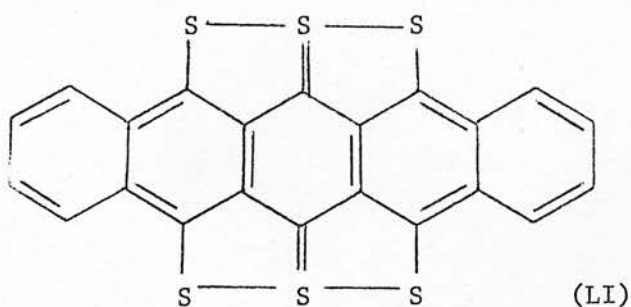


in the synthesis of compounds containing dithiole ring systems fused to pentacene (L) and hexacene (LII), the higher homologues of tetracene in the "polyacene series".

The reaction of pentacene (L), which has six reactive meso-

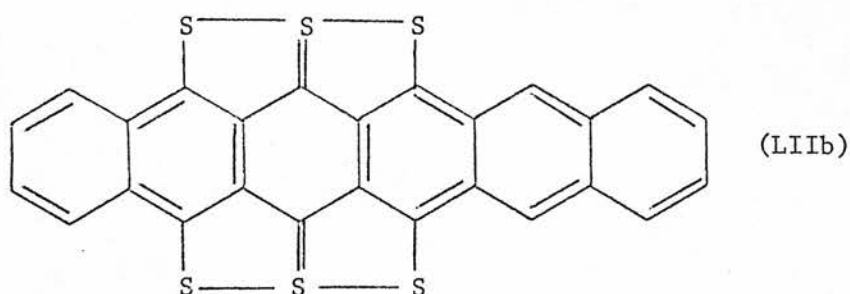
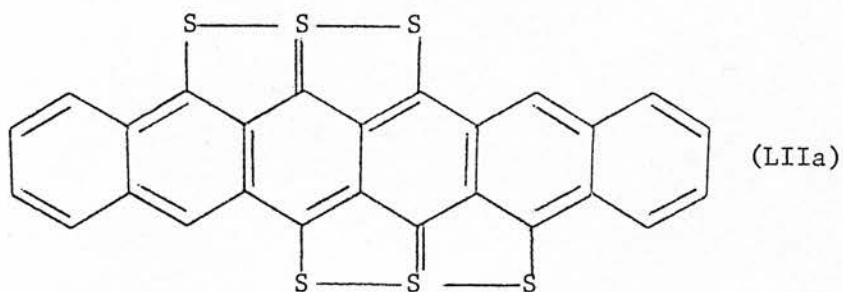


positions, with elemental sulphur is reported to produce hexathio-pentacene and the formula (LI) is suggested as the most likely possibility. The electrical properties of this compound were measured and it was shown to be an insulator ( $\sigma_{20} = 1.2 \times 10^{-13}$  ohm<sup>-1</sup> cm<sup>-1</sup>).<sup>(45)</sup> Attempts to produce a radical-cation failed, and its lack of conductivity and inertness to oxidation are attributed to the enhanced stability conferred by the presence of two thiathiophthen systems which, unlike the dithiole ring, do not require the removal of an electron in order to become aromatic.

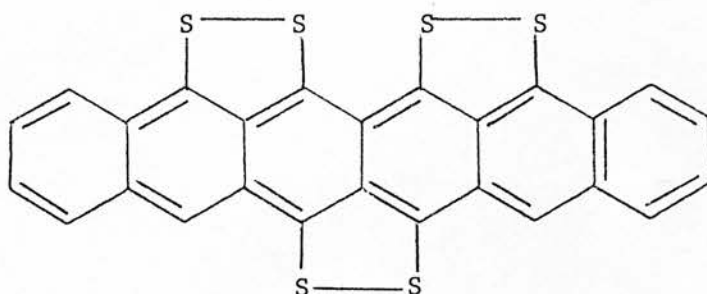


Hexacene (LII), which has eight reactive positions, did not form an octasulphide, on reaction with elemental sulphur under the same conditions as for pentacene. Instead, a compound showing  $m/e$  514, corresponding to a hexasulphide, was isolated. The electrical

conductivity of the compound ( $\sigma_{20} = 8.3 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) was measured but no p.m.r. spectrum was obtained owing to its insolubility. Possible structures are (LIIa) and (LIIb), each containing two thiathiophthen units,



but, by analogy with hexathiopentacene such a structure might be expected to give rise to a low conductivity. On the other hand, if the structure (LIII) was formed, then the conductivity would be expected to be higher, by analogy with tetrathiotetracene, and oxidation to the radical cation should be possible. Perhaps



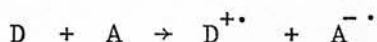
(LIII)

the most satisfactory explanation would be that the main component is the bithiathiophthen and that a small amount of (LIII) is also present, thus accounting for the higher conductivity.

The failure to obtain octathiohexacene by the reaction of hexacene with elemental sulphur could then be attributed to the stability of the thiathiophthen ring system, for if the replacement of the mesohydrogens occurs in a stepwise mode, then formation of the octasulphide will necessarily proceed via the hexasulphide and, either because of insolubility of the latter, or because it is relatively inert, the reaction does not proceed further. (51)

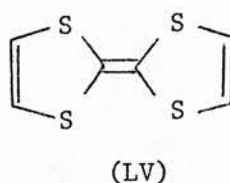
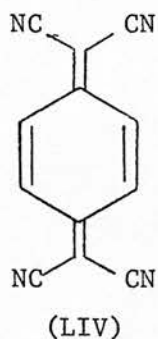
### Solid State Conductivity

The electrical conductivities of the compounds mentioned above are in the semiconductor to insulator range. Higher conductivities are continually being sought, however, and recent studies have shown that the metallic state can be achieved in certain organic charge transfer salts.<sup>(52)</sup> In contrast to conventional molecular crystals (composed of neutral organic molecules held together by Van der Waals forces) charge transfer salts have unpaired electrons on the acceptor (A) or donor (D), or both, as a result of the electron transfer.



If, in the resulting compound, the unpaired electrons delocalise over all molecular sites then the metallic state results, if the electrons localise in individual sites then a paramagnetic insulator may result.

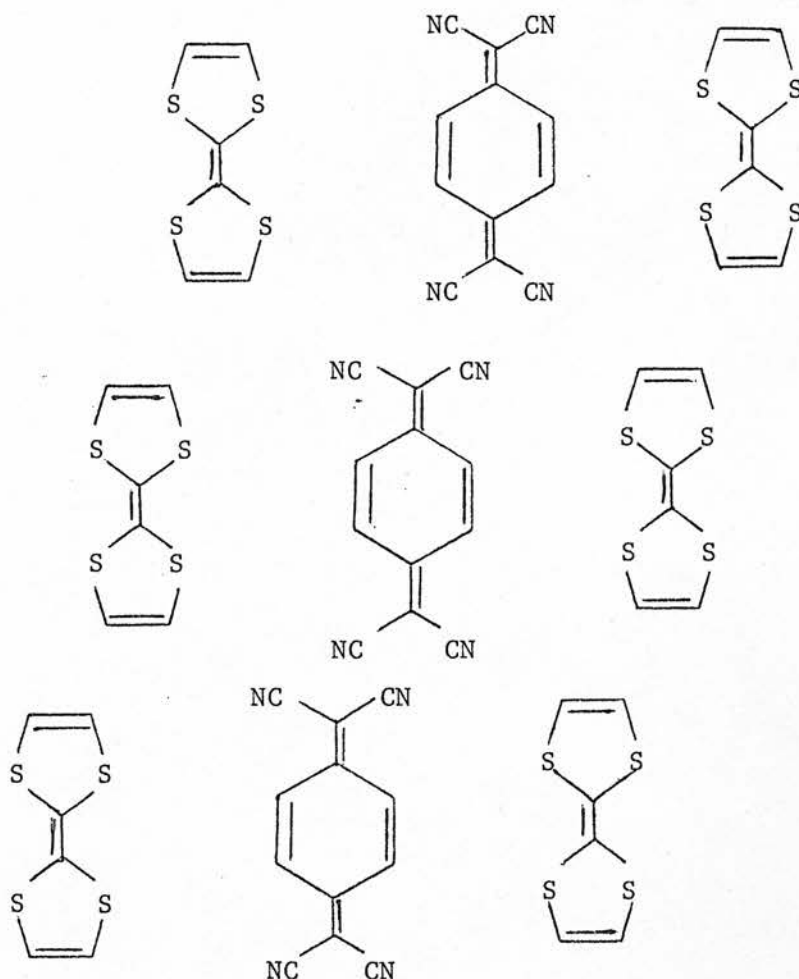
The main characteristic of metallic behaviour is a large electrical conductivity which decreases with increasing temperature. Well studied examples<sup>(52)</sup> of this type are the charge transfer salts of tetracyanoquinodimethane (TCNQ) with bis(1,3-dithiol-2-ylidenes). (Sometimes known as "tetrathiafulvalenes" (TTF)).



These salts crystallise as segregated one-dimensional stacks



of donors and acceptors within the crystal lattice and an X-ray analysis<sup>(53)</sup> shows parallel uniform chains as indicated below.

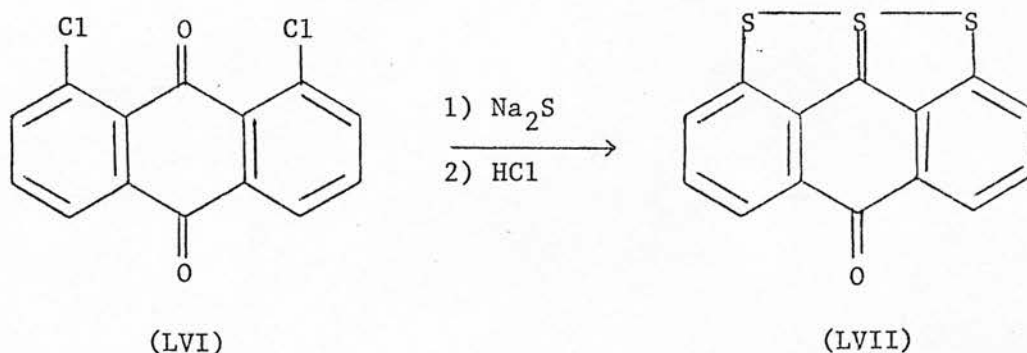


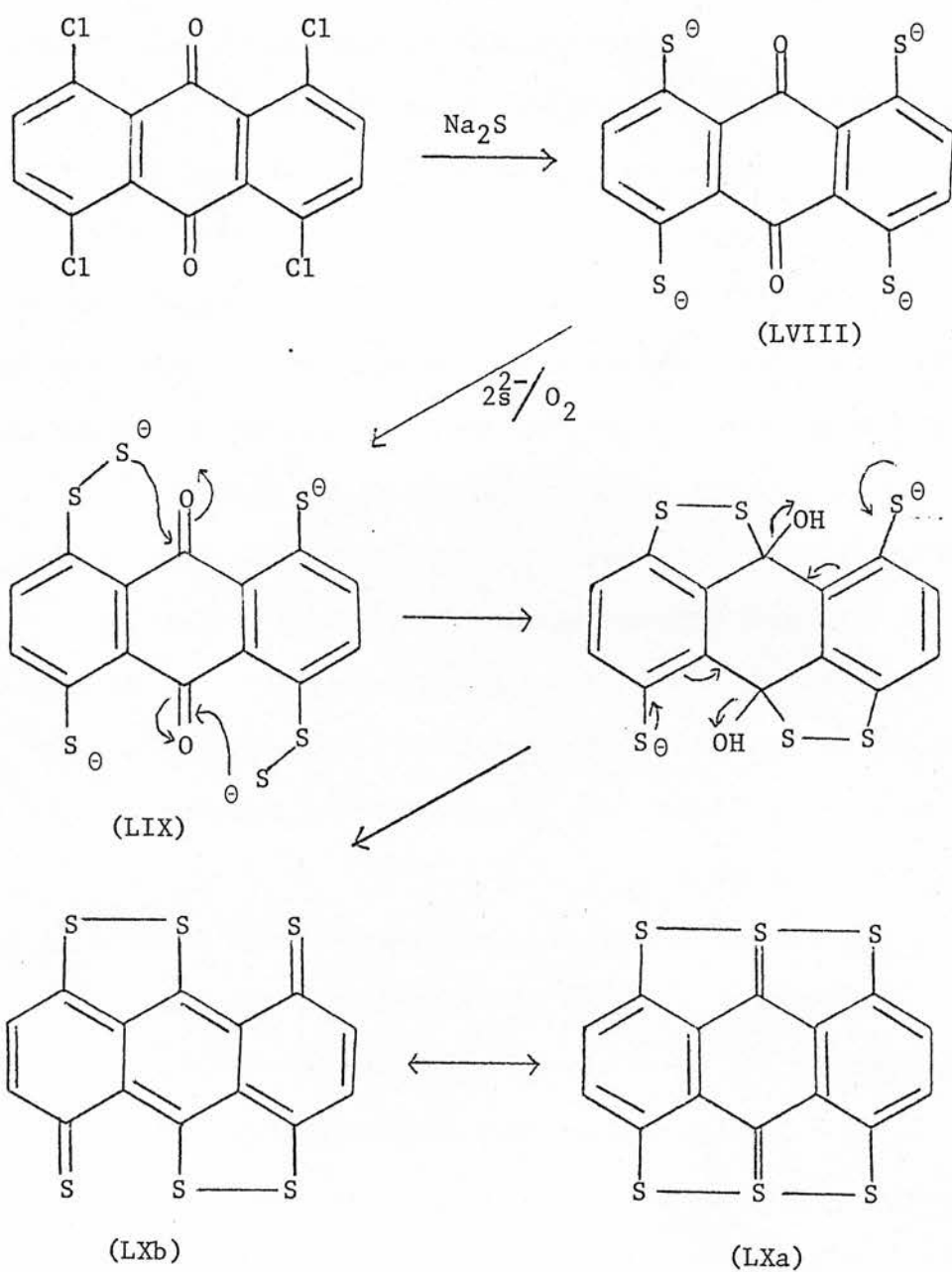
The salt  $\text{TTF}^+ \text{TCNQ}^-$  as single crystals<sup>(54)</sup> showed highly anisotropic metallic conductivity which increased from  $10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$  at room temperature to a maximum of  $1.5 \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $66^\circ\text{K}$  the highest value recorded for an organic material, then at  $58^\circ\text{K}$  it underwent a metal-insulator transition. But a remarkable feature was observed, that a few crystals (three out of the original seventy) showed an enormous increase in conductivity before the

transition to above  $10^6 \text{ ohm}^{-1} \text{ cm}^{-1}$ . This exceeds the conductivity of copper at room temperature and has been attributed to fluctuations that herald superconductivity. These samples are however not reproducible and no other worker has observed these giant conductivity peaks.

The initial observations of solid-state conductivity in tetrathiotetracene and related compounds provided the basis for a programme of research, in this department, aimed at the synthesis of other polycyclic compounds containing 1,2-dithiole rings. This programme, which was started by S. Davidson, has been carried out as a Science Research Council CAPS (CASE) project in collaboration with the ICI Corporate Laboratory. It was intended that any new systems synthesised in Edinburgh should be submitted to the Corporate Laboratory for conductivity measurements should these seem desirable.

Davidson planned first to synthesise 5-oxo-5H-anthra(1,9,8-bcde) thiathiophthen (LVII) "trithioanthrone" from 1,8-dichloroanthraquinone (LVI) by conversion to the 1,8-dimercapto-compound and treatment of this with phosphorus pentasulphide. Surprisingly, however, the desired compound was obtained directly by acidification of the solution produced by boiling 1,8-dichloroanthraquinone with sodium sulphide in dimethylformamide.

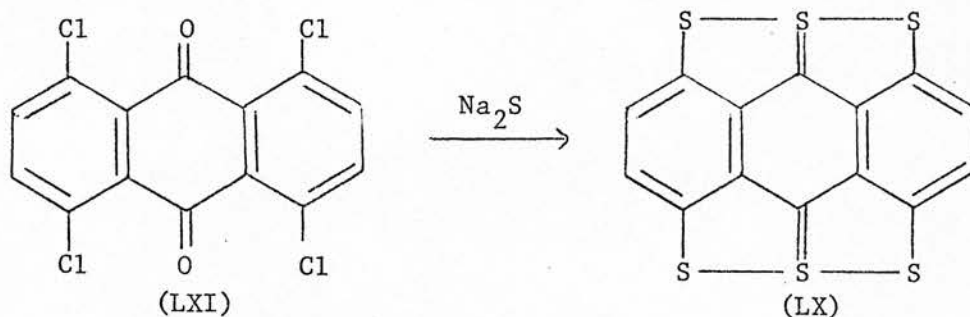




Scheme 6

The compound was characterised by mass spectroscopy, elemental analysis, and p.m.r. (the low solubility of the compound necessitating the use of hot 1,1,2-trichloroethane as solvent). Trithioanthrone was not tested for conductivity; it was shown to act as a green dye on Nylon yarn but the colour was not fast to light.

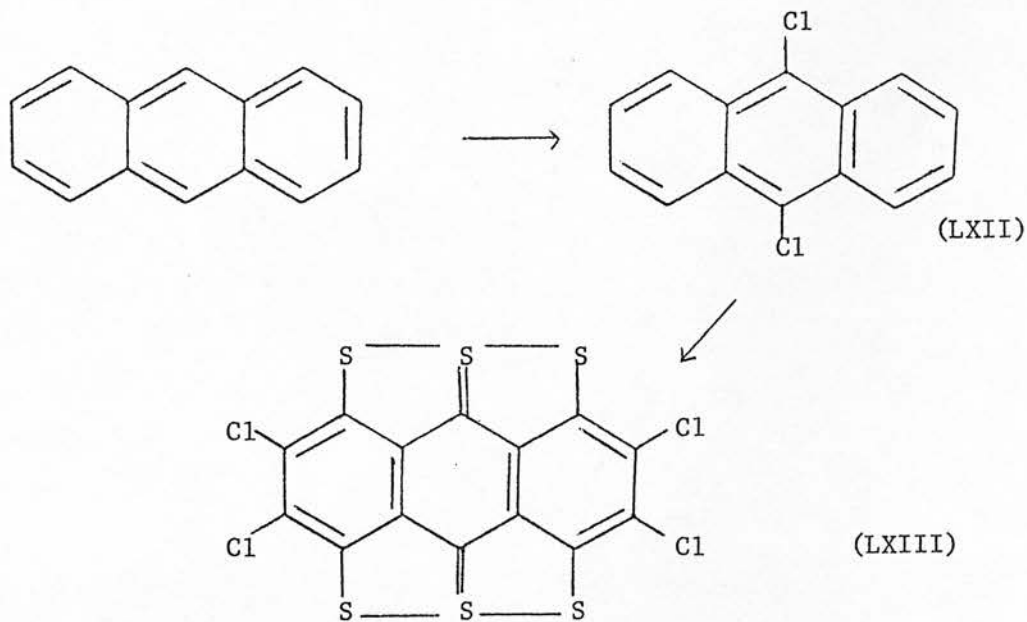
Anthra(1,9,8-bcde : 5,10,4-b'c'd'e') bis(thiathiophthen) (LX) ("hexathioanthracene") was also prepared by a similar reaction from 1,4,5,8-tetrachloroanthraquinone (LXI), and was obtained as a green microcrystalline solid with a metallic lustre.



Evidence for the proposed structure of this compound was notably incomplete, being based solely on its mass spectrum and exact mass measurement ( $\text{C}_{14}\text{H}_4\text{S}_6$ ) since Davidson could not obtain an analytically pure sample. No n.m.r. evidence was available since the compound was insufficiently soluble.

The mode of formation is postulated as shown opposite (scheme 6). Nucleophilic displacement of chlorine yields the anthraquinonetetrathiolate anion (LVIII) which, by oxidative reaction with further sulphide ion, yields the species (LIX). Ring closure and expulsion of two hydroxide ions would then give "hexathioanthracene" (LXa,b) (two canonical structures shown).

Prior to Davidson's synthesis, the ring system of "hexathioanthracene" had not been recognised as existing. In 1930, however, von Weinberg<sup>(55)</sup> isolated a compound with the empirical formula  $C_{14}Cl_4S_6$  from the reaction between anthracene and sulphur monochloride and this could possibly have been the tetrachloro-derivative (LXIII) of hexathioanthracene. This reaction was reinvestigated by S. Davidson,<sup>(29)</sup> using boiling 1,2,4 trichlorobenzene as reaction medium, and the first product isolated was 9,10-dichloroanthracene (LXII). Prolonged reaction produced the compound described by von Weinberg and in an independent reaction, 9,10-dichloroanthracene with sulphur monochloride gave the same product. The product was a green microcrystalline powder, similar in appearance to hexathioanthracene, and mass spectrometry confirmed the molecular formula.

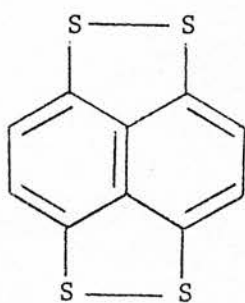


The initial isolation of 9,10-dichloroanthracene (LXII) is analogous to the isolation of 9,11-dichlorotetracene by Marschalk<sup>(37)</sup>

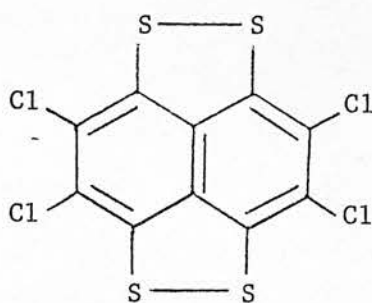


as an intermediate in the preparation of tetrathiotetracene (XXXIII).

Naphtho[1,8-cd : 5,4-c'd']bis[1,2] dithiole (LXIV) which is closely related to tetrathiotetracene (XXXIII), and may therefore show interesting electrical properties, is not a known compound but the tetrachloro derivative (LXV) has recently been reported by Klingsberg<sup>(56)</sup> who obtained it by fusion of octachloronaphthalene



(LXIV)



(LXV)

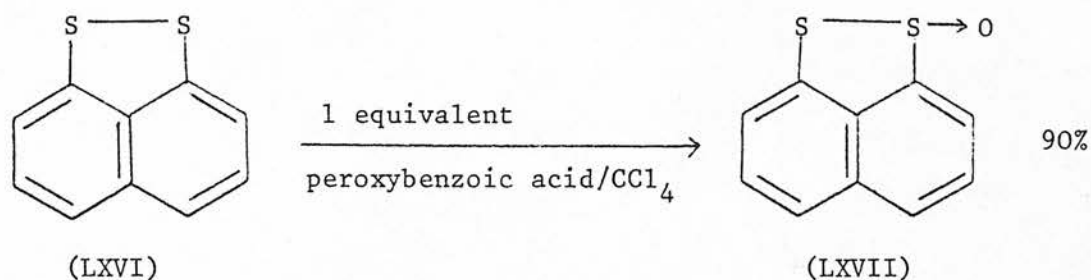
with elemental sulphur at 310°.

Naphthalene-1,8-disulphide (XLVI) has been known much longer and was first prepared by Lanfrey<sup>(57)</sup> who caused naphthalene and sulphur to interact in a hot iron tube. Price and Smiles<sup>(58)</sup> reported a more rational synthesis from 1-aminonaphthalene-8-sulphonic acid (LXVIa) and this basic route has now been optimised by Zweig and Hoffmann<sup>(59)</sup> as shown opposite (scheme 7)

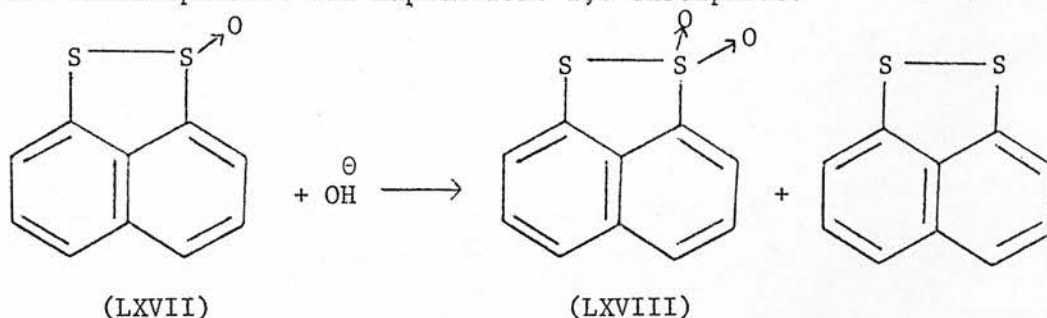
The disulphide forms charge transfer complexes with 2,3-dichloro-5,6-dicyano-p-benzoquinone, tetracyanoethylene and p-chloranil<sup>(59)</sup>, and reacts with sulphuric acid to produce the radical-cation which has been studied by e.s.r.<sup>(59)(60)</sup> and ultraviolet spectroscopy. The radical-cation is also formed by treatment with aluminium chloride in nitromethane.<sup>(61)</sup>

Naphthalene-1,8-disulphide is oxidised by sodium metaperiodate or peroxybenzoic acid to the corresponding thiosulphinate and

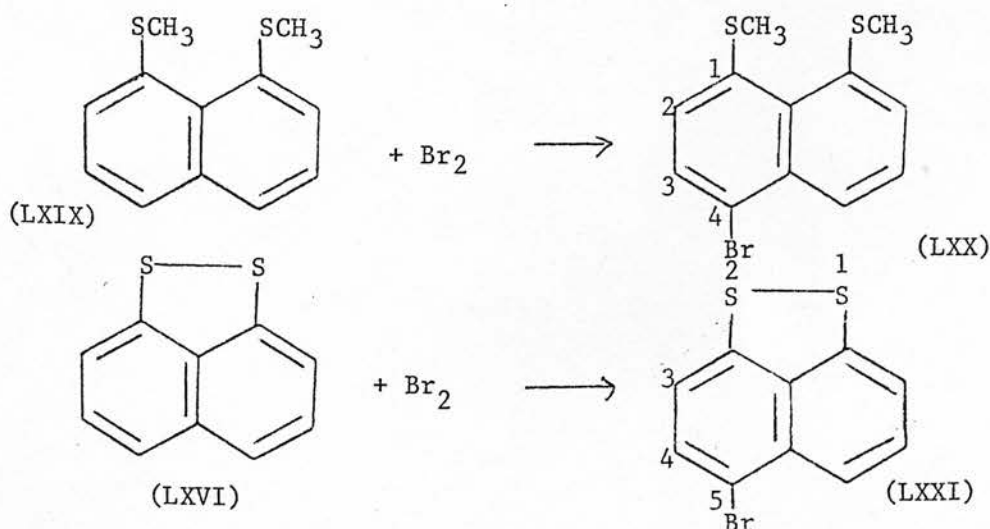
this can be further oxidised to the thiosulphonate. (62)



Hydrolysis of the thiosulphonate has been reported by Tamagaki<sup>(62)</sup> to follow 2nd order kinetics forming a mixture of the thiosulphonate and naphthalene-1,8-disulphide.



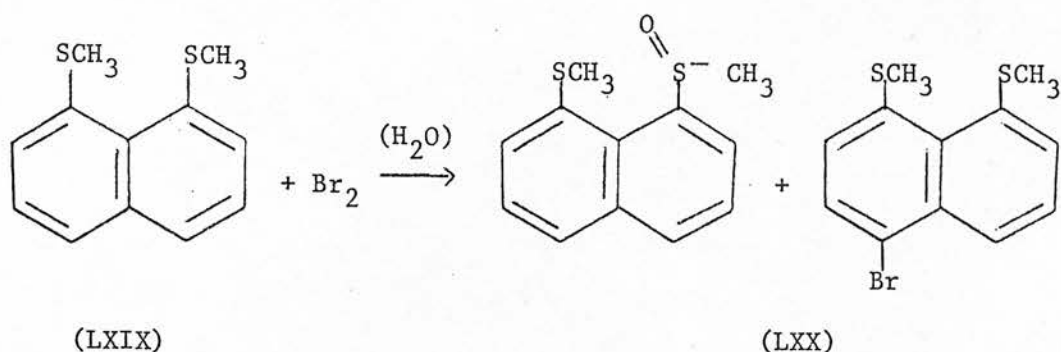
Naphthalene-1,8-disulphide and the open chain analogue (LXIX), formed by reaction of the disulphide with dimethyl sulphate react quickly with bromine in carbon tetrachloride-acetic acid at room temperature giving an almost quantitative yield of the corresponding p-monobromoderivatives.



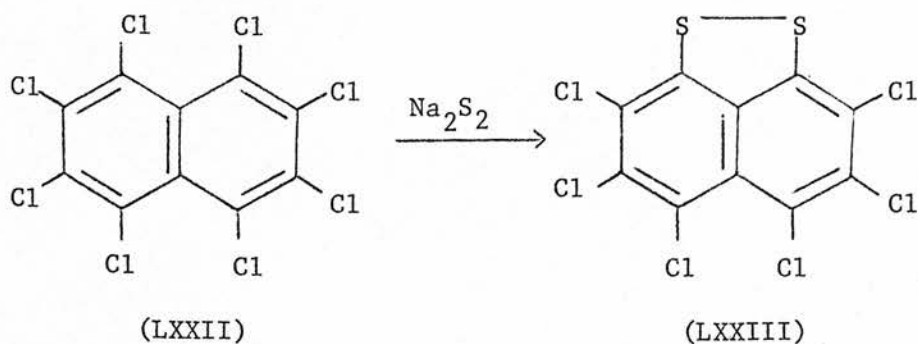


This behaviour with a typical electrophilic reagent confirms experimentally what has been predicted for the parent<sup>(63)</sup> compound (LXVI) and provides a convenient route to the compounds (LXX) and (LXXI) which are not otherwise easily available. The reaction with the disulphide appears to occur by direct bromination at the 5-position and not, as in the corresponding reaction of 1,8-di-(methylthio)naphthalene, through a bromosulphonium cation.

When the bromination is carried out in the presence of water (5 mol) the same reaction occurs with the 1,8-disulphide but the 1,8-di(methylthio)-compound gives a mixture of the 4-bromo derivative, and the monosulphoxide.



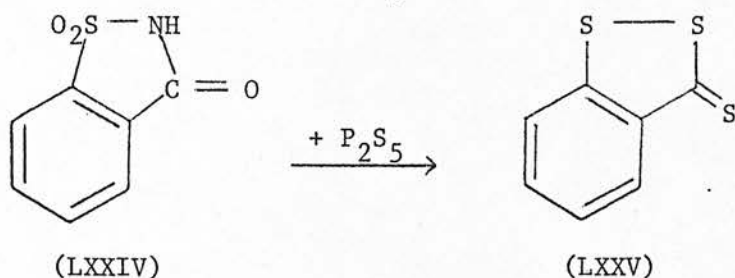
The hexachloro derivative of naphthalene-1,8-disulphide (3,4,5,6,7,8-hexachloronaphtho[1,8-cd]-1,2-dithiole) (LXXIII) has been reported by Thelin<sup>(64)</sup> in the patent literature as an intermediate in the preparation of naphthalene-1,8-disulphide from octachloronaphthalene, (LXXII)



and recently Klingsberg<sup>(65)</sup> has reported its oxidation by chromium trioxide to 3,4,5,6,7,8-Hexachloronaphtho[1,8-cd]-1,2-dithiole-1-oxide.

When the present investigation began no compounds were known in which more than one 1,2-dithiole ring was fused to a benzene ring. Very recently however J.P. Brown has reported the synthesis of a compound containing three 1,2-dithiole rings fused to a benzene nucleus<sup>(66)</sup> (see discussion).

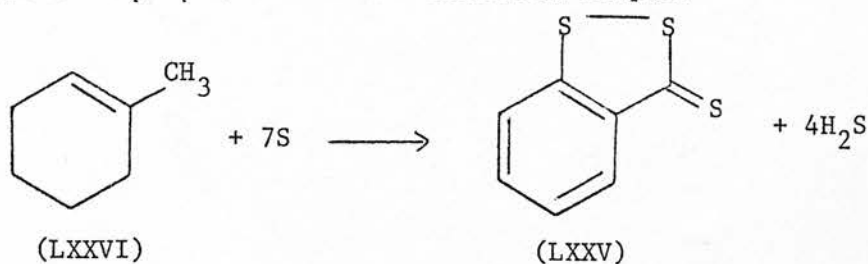
Benzodithiolethiones however, are well known, the parent compound having been first obtained by Manessier in 1916 from saccharin (LXXIV) by reaction with phosphorus pentasulphide.<sup>(67)</sup>



Although the yield is small the reaction is of some historical importance because the product is apparently the first dithiolethione to have been correctly described.

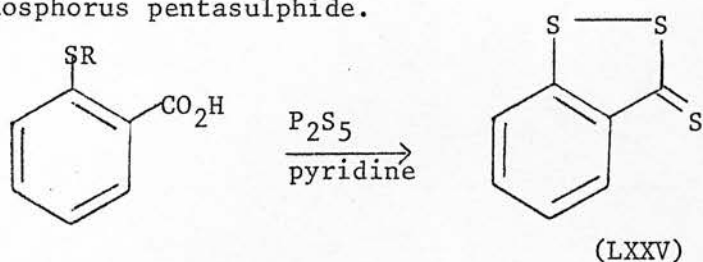
Since then many methods of synthesis have become available of which the most generally useful are:-

- a) From methylcyclohexene and elemental sulphur<sup>(68)</sup>



The reaction involves heating a mixture of methylcyclohexene (LXXVI) and elemental sulphur at 200°. In addition to forming the 1,2-dithiole-3-thione, a common mode of reaction with olefins, the sulphur also acts as a dehydrogenating agent for aromatisation of the six-membered ring.

- b) From o-mercaptobenzoic acid (or its disulphide)<sup>(69)</sup> and phosphorus pentasulphide.

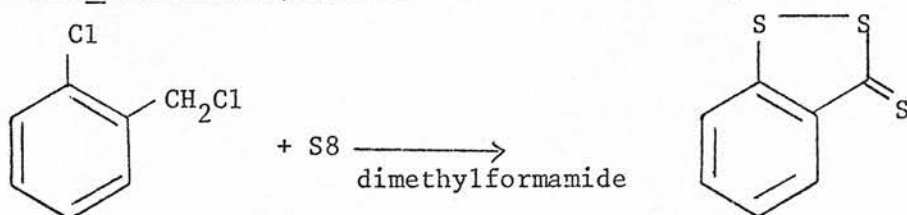


1) R = H

2) R = o - s - C<sub>6</sub>H<sub>4</sub>.CO<sub>2</sub>H

This method gives the benzodithiolethione (LXXV) in one step.

- c) From o-chlorobenzylchloride and elemental sulphur.<sup>(70)</sup>

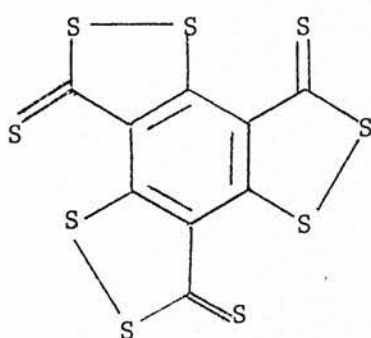


This method, recently introduced by Brown, involves heating the reactants for 40h. in boiling dimethylformamide.

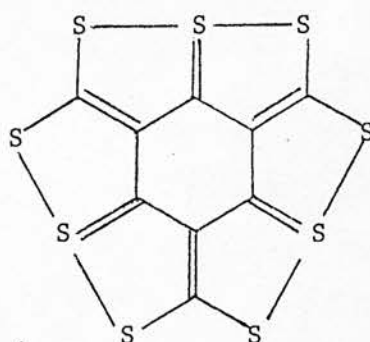
DISCUSSION

1. Compounds Containing two or more 1,2-dithiole Rings Fused to a Benzenoid Nucleus

Of the several compounds theoretically possible within this general class, two are of particular interest since they consist entirely of carbon and sulphur atoms and each can be represented by two or more types of valence-bond structures. Compound (LXXVIII,a,b)  $C_9S_9$  is based on the carbon skeleton of mesitylene and compound (LXXIXa,b,c),  $C_8S_8$  is based on that of p-xylene.

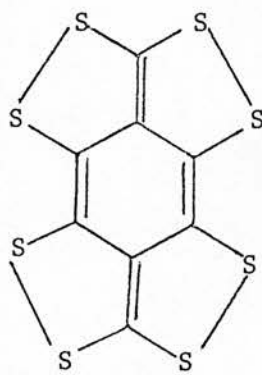


(LXXVIIIa)

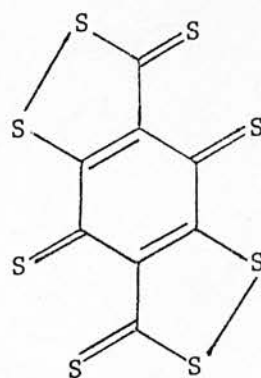


(LXXVIIIb)

or

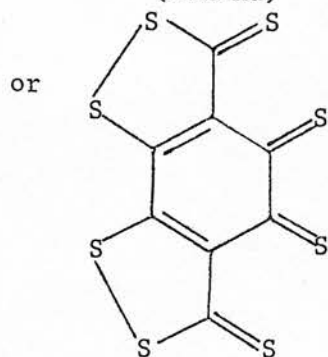


(LXXIXa)



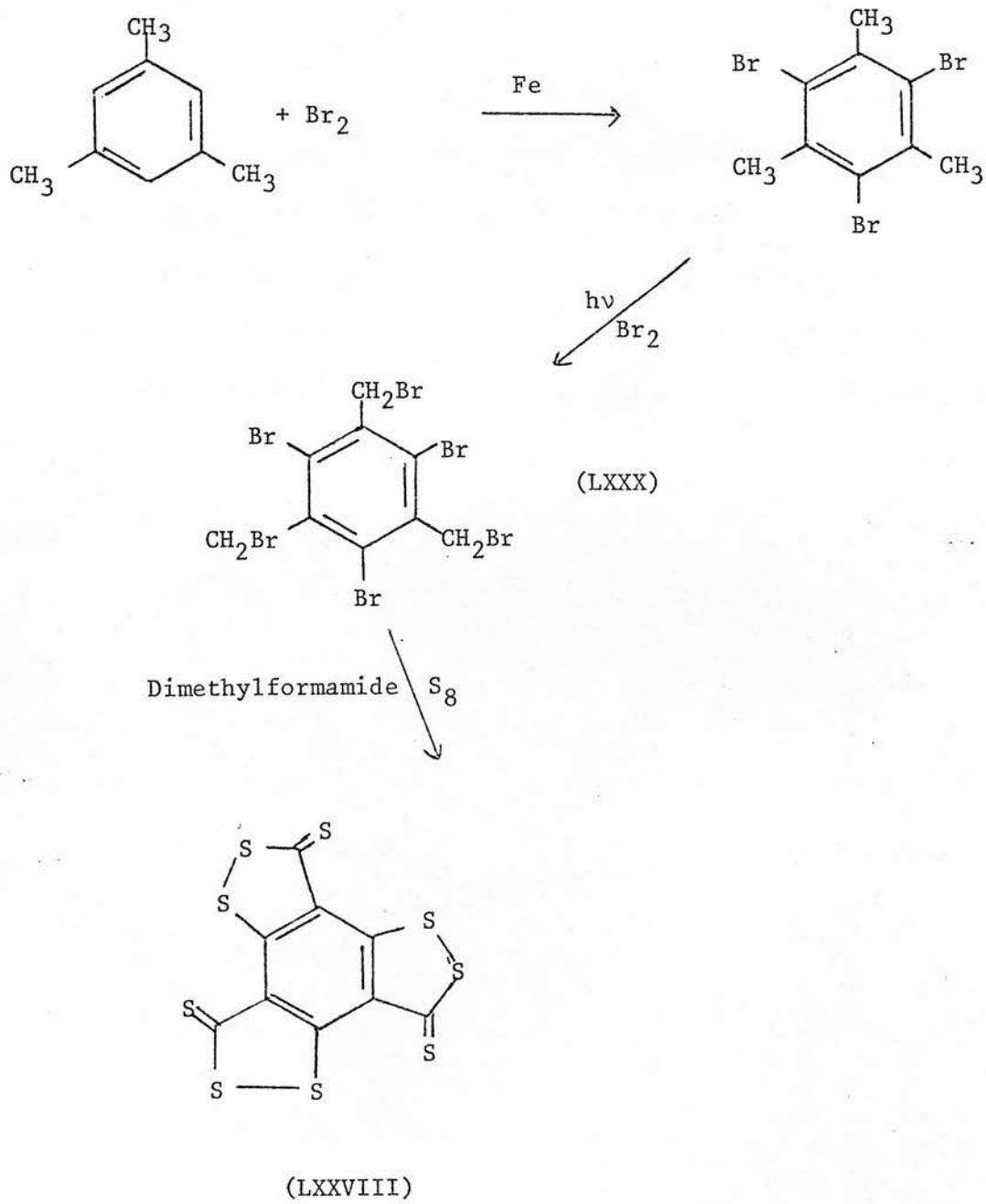
(LXXIXb)

or



(LXXIXc)

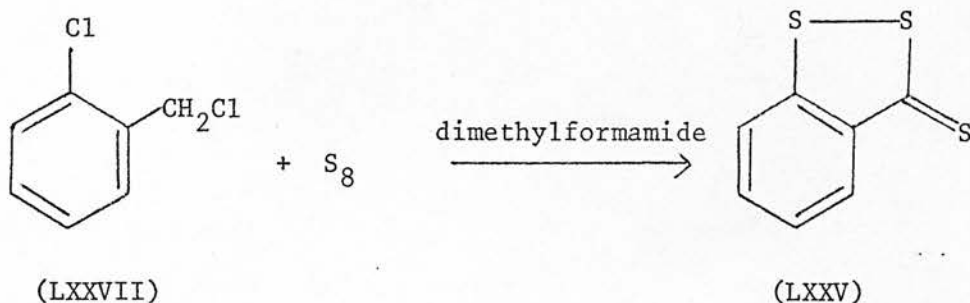
or



Scheme 8

(a) Preparation of a Sulphocarbon containing the Mesitylene Carbon Skeleton -  $C_9S_9$ .

An approach to the sulphocarbon (LXXVIII) was based on information received privately from Dr J P Brown that benzo-1,2-dithiole-3-thione (LXXV) could be obtained by heating *o*-chlorobenzyl chloride with elemental sulphur in dimethylformamide.



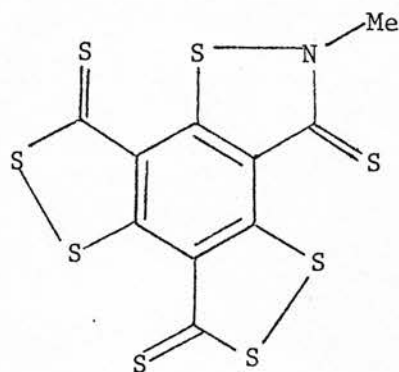
This observation suggested that the analogous polyhalogenated mesitylene (LXXX) would be an ideal precursor for the synthesis of benzo[1,2-c; 3,4-c'; 5,6-c''] tris[1,2]dithiole-1,4,7-trithione (LXXVIII).

Treatment of mesitylene with bromine, using iron as catalyst,<sup>(71)</sup> produced 1,3,5-tribromomesitylene which, by photochemically initiated bromination in carbon tetrachloride, gave the desired product, 1,3,5-tribromo-2,4,6-tris(bromomethyl)benzene (Scheme 8). The presence of a singlet ( $\tau = 5.10$ ) in the p.m.r. spectrum and a mass spectrum which showed a series of parent molecular ions ranging from  $m/e$  588 to  $m/e$  600 (6 Br isotope pattern) confirmed the identity of the product. No attempt was made to obtain an analytically pure specimen since it was expected that any impurity containing more than six bromine atoms would react with sulphur in the same way as the hexabromo compound.

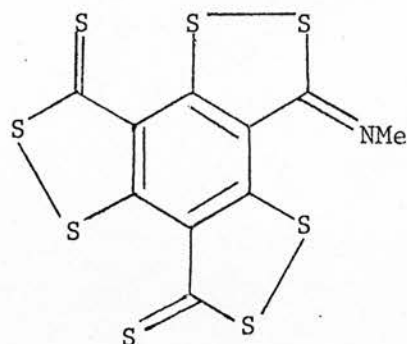
The hexabromomesitylene (LXXX) was heated under reflux with elemental sulphur and dimethylformamide for seven days during which time a product separated from the reaction mixture as an insoluble brown solid. The mass spectrum of the solid (at 300°C) showed a parent ion corresponding to the desired product  $C_9S_9$  ( $m/e$  396) but the presence of other peaks which were clearly not fragment ions ( $m/e$ : 393, 390, 387) suggested that nitrogenous compounds were present in which one, two or three S atoms of  $C_9S_9$  were replaced by N-Me groups derived from the solvent.

The  $m/e$  393 product, for example, might be represented by either of the structures (LXXXIa) or (LXXXIb) or by a structure (LXXXII) containing trithiapentalene and dithia-azapentalene systems.

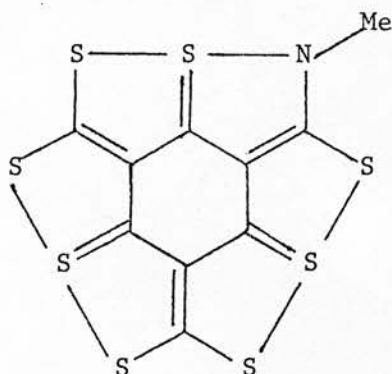
$m/e$  393



(LXXXIa)



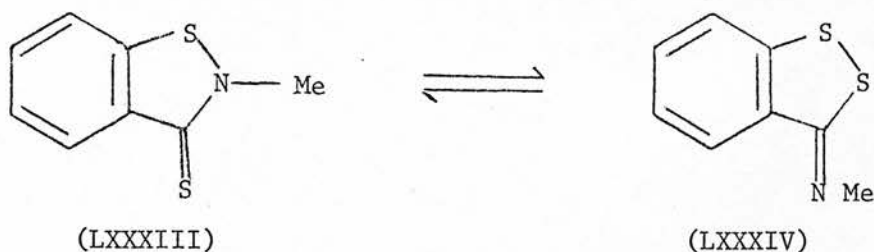
(LXXXIb)



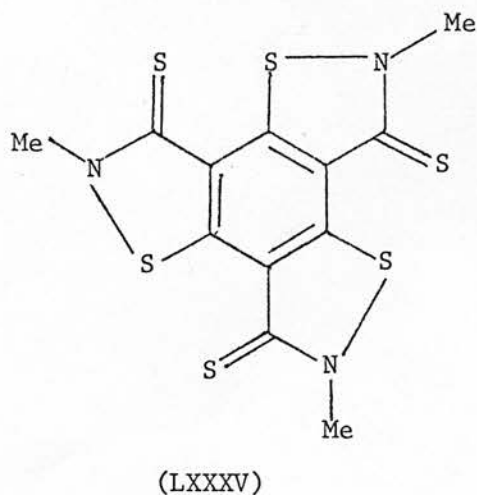
(LXXXII)

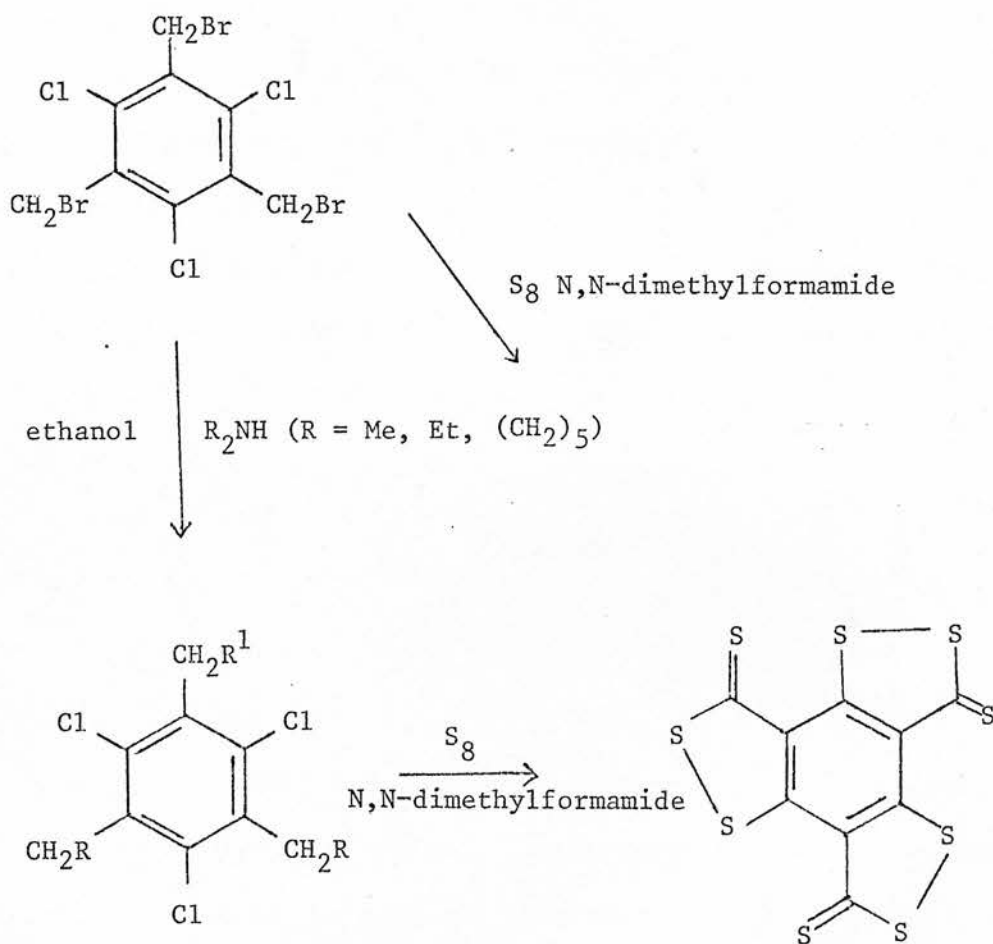


Bøshagen and his coworkers<sup>(72)</sup> have shown that benzo-1,2-dithiole-3-thione reacts with aliphatic amines to give N-alkyl-benzisothiazolinethiones (LXXXIII) which are tautomeric with the corresponding benzo-dithiolimines (LXXXIV) and it seems likely that a similar process involving methylamine (from decomposition of dimethylformamide) and the sulphocarbon (LXXXVIII) is responsible for the formation of these nitrogenous by-products.



Attempts to obtain the pure compound  $C_9S_9$  by crystallisation from common organic solvents failed. Sublimation under high vacuum yielded a red solid, the mass spectrum of which (run under the same conditions as the crude material  $C_9S_9$ ) showed a decrease in intensity of the peaks at  $m/e$ : 396, 393 and 390 and an increase in the intensity of the peak at  $m/e$  387. This last peak was the most abundant in the spectrum and was probably due to the benzotrisisothiazole derivative (LXXXV) or a valence tautomer.





$\text{R}^1 = \text{N.Me}_2$   
 $= \text{piperidino}$   
 $= \text{N.Et}_2$

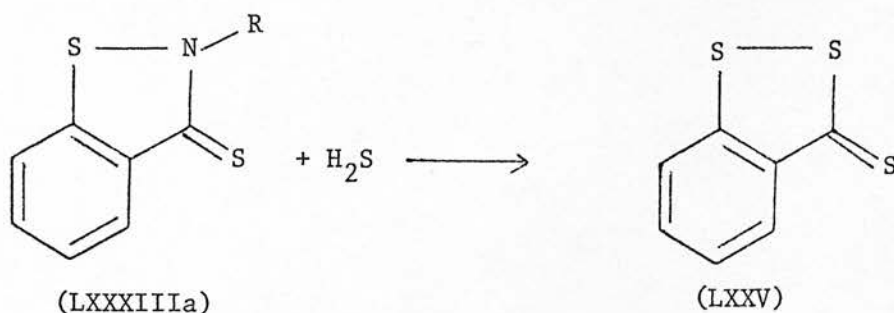
SCHEME 9

The base peak in the mass spectrum obtained from the crude  $C_9S_9$  occurred at  $m/e$  320, corresponding to loss of  $CS_2$  from the parent ion (confirmed by a metastable ion peak at  $m/e$  250.8).

At this stage in the investigation, Dr J P Brown kindly informed us that he had been carrying out similar experiments aimed at the synthesis of  $C_9S_9$  and had encountered similar problems with nitrogenous contaminants. In view of the fact that Brown's work had progressed slightly further it seemed prudent to discontinue our parallel investigations. A summary of Brown's findings, as later published, is now presented.

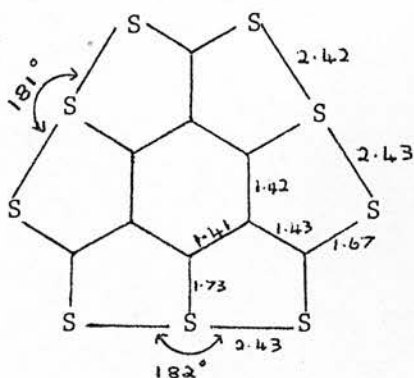
Brown<sup>(66)</sup> used the more soluble triamines (Scheme 9) as starting materials and, by heating with sulphur in dimethylformamide, obtained a product which consisted mainly of the sulphocarbon,  $C_9S_9$  contaminated with a nitrogen compound, ( $m/e$  393) for which the structure (LXXXI) was suggested.

Since hydrogen sulphide<sup>(73)</sup> is known to react with 2-alkylbenz-isothiazoline-3-thiones (LXXXIIIa) to form benzo-1,2-dithiole-3-thiones (LXXV), Brown attempted to suppress the production

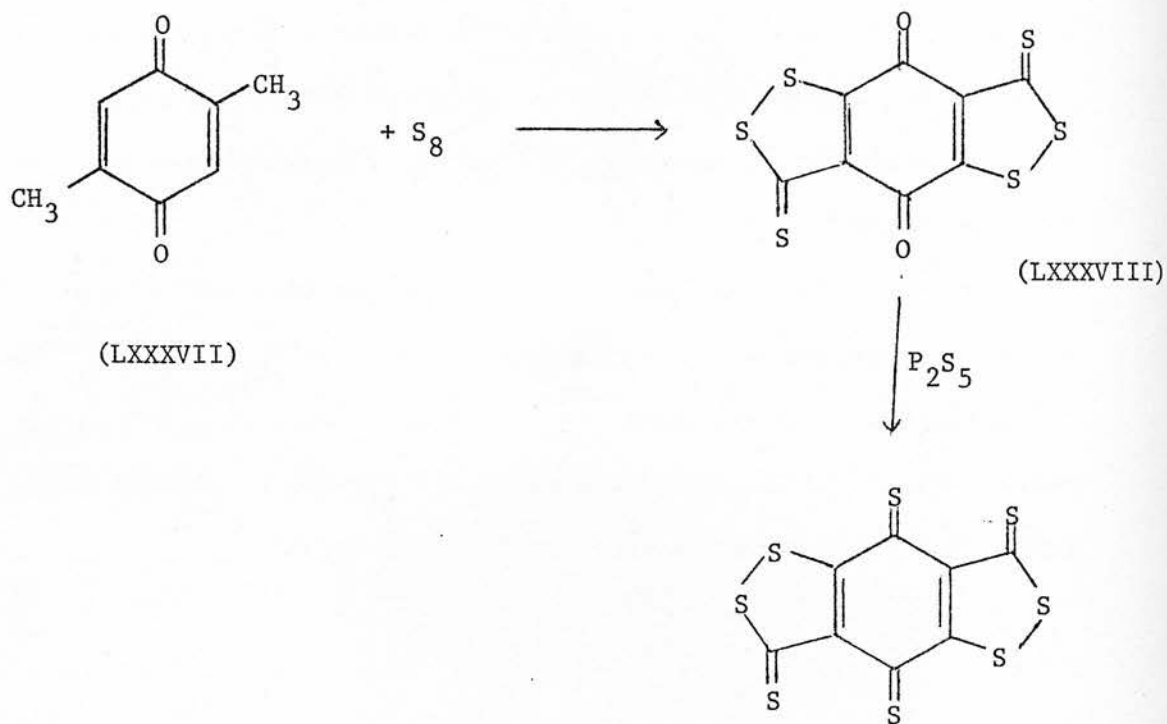


of (LXXXI) by bubbling hydrogen sulphide through the reaction mixture during the reflux period. Some decrease in the amount of nitrogen-containing compound was observed and a very small yield of analytically pure  $C_9S_9$  was obtained by slow crystallisation from quinoline.

Recently the X-ray crystal structure has been determined<sup>(74)</sup> and shows the compound to be essentially planar with  $D_{3h}$  symmetry. The S-S distances indicate delocalised bonding in each of the linear three-sulphur systems but these distances ( $2.43\text{\AA}$ ) are longer than those which were found in 6a-thiathiophthen ( $2.36\text{\AA}$ ).



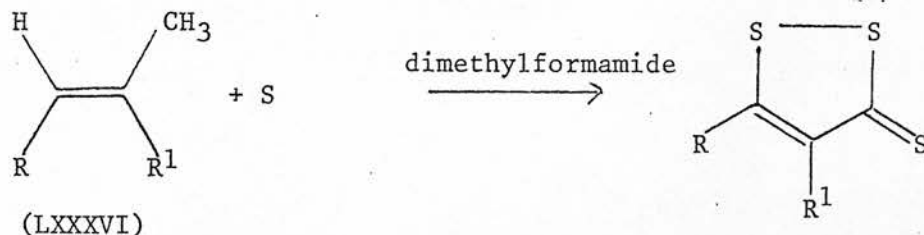
Thus the sulphocarbon is related to the hydrocarbon coronene in the same way that 6a-thiathiophthen is related to naphthalene.



Scheme 10

(b) The Attempted Preparation of a Sulphocarbon Containing the p-Xylene carbon skeleton - C<sub>8</sub>S<sub>8</sub>

One of the most common synthetic routes to substituted 1,2-dithiole-3-thiones is the reaction between an appropriately substituted propene (LXXXVI) and elemental sulphur.<sup>(75)</sup> This reaction is not inhibited by the presence of a carbonyl substituent (e.g. R = Ph; R<sup>1</sup> = Ph.CO) and proceeds normally (though with subsequent dehydrogenation) when R and R<sup>1</sup> are part of a six-membered ring. (i.e. with 1-methylcyclohexene).<sup>(68)</sup>



Based on these observations, a route to the sulphocarbon, C<sub>8</sub>S<sub>8</sub> was envisaged, starting from 2,5-dimethyl-p-benzoquinone as outlined in Scheme 10.

The reaction of 2,5-dimethyl-p-benzoquinone (LXXXVII) with elemental sulphur was first carried out in dimethylformamide. The reaction mixture quickly turned dark and a black glassy solid was formed over the period of reflux.

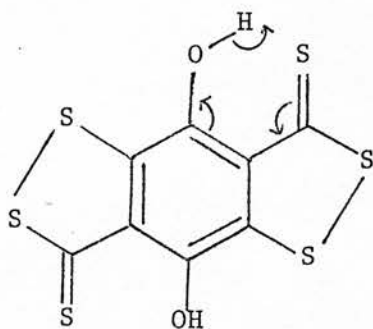
The solid, which constituted a large percentage of the total weight of reactants, was insoluble in a range of organic solvents and could not be purified. It was heated to 300°C in the mass spectrometer but the only spectrum which could be obtained was that of elemental sulphur. The residue which remained on the probe was difficult to burn completely. A similar black solid was obtained

when the reaction was carried out in dimethyl sulphoxide.

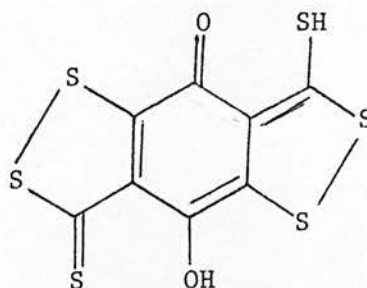
The same reaction was repeated using ethyl benzoate as solvent and when t.l.c. showed that all the starting material had reacted, the reaction mixture was cooled and a dark solid was filtered off. The solid proved to be quite insoluble in most solvents but a mass spectrum of the crude material showed a parent ion peak at  $m/e$  322, the value for the desired quinone (LXXXVIII) being  $m/e$  320. This result suggested the presence of a compound of molecular formula  $C_8H_2O_2S_6$  which was confirmed by exact mass measurement.

The solid was then extracted continuously with hot acetone in a Soxhlet apparatus and sufficient of a dark green solid was obtained for one recrystallisation from ethyl benzoate. The analytical results indicated however, that the sample still contained a small amount of impurity.

Owing to low solubility a p.m.r. spectrum could not be obtained but the compound is likely to possess one of the tautomeric structures shown below (LXXXIXa,b)



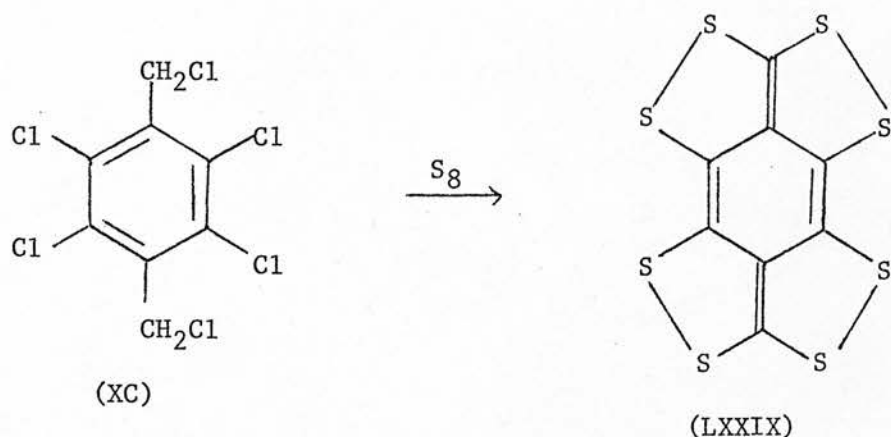
(LXXXIXa)



(LXXXIXb)

The mass spectrum showed a loss of 33 mass units (SH) from the parent ion which was confirmed by the presence of a metastable peak. This would seem to provide support for the second structure (LXXXIX,b) but there is the possibility of the form (LXXXIXa) undergoing rearrangement by the route shown to form (LXXXIXb) within the mass spectrometer.

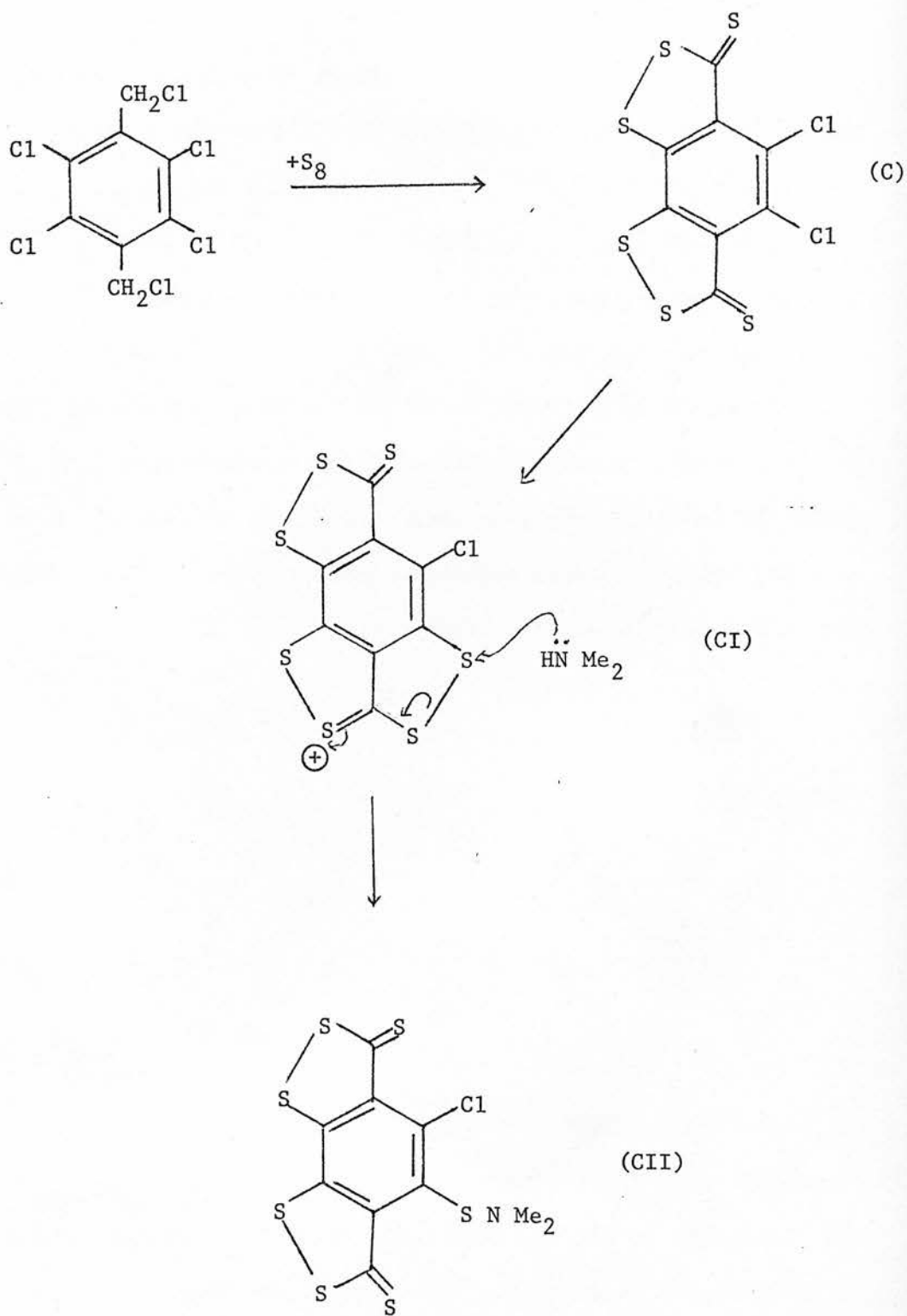
An alternative route to the sulphocarbon (LXXIX) was based on the partially successful route to the sulphocarbon,  $C_9S_9$  (LXXVIII) from the polyhalogenated mesitylene (LXXX). In this case the polyhalogenated precursor was  $\alpha,\alpha',2,3,5,6$ -hexachloroxylene (XC) which is commercially available.



Heating under reflux with sulphur in dimethylformamide and chromatographic separation yielded several products none of which was present in sufficient amount for adequate characterisation.

The first product obtained from the chromatography column by elution with light petroleum was a high melting purple solid whose mass spectrum showed a parent ion peak at  $m/e$  399. The fact that this is an odd number indicated the presence of nitrogen and pointed once again to solvent participation in the reaction.



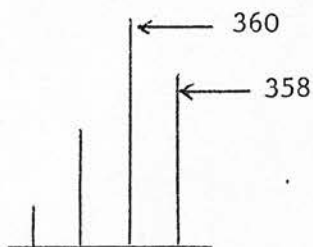


Scheme 11

Metastable peaks confirmed the loss of fragments of 15 ( $\text{CH}_3$ ) and 35 (Cl) mass units and exact mass measurement on the parent ion peak showed the molecular formula of this product to be  $\text{C}_{10}\text{H}_6\text{Cl N S}_7$  (The  $^{37}\text{Cl}$  isotope peak was also present).

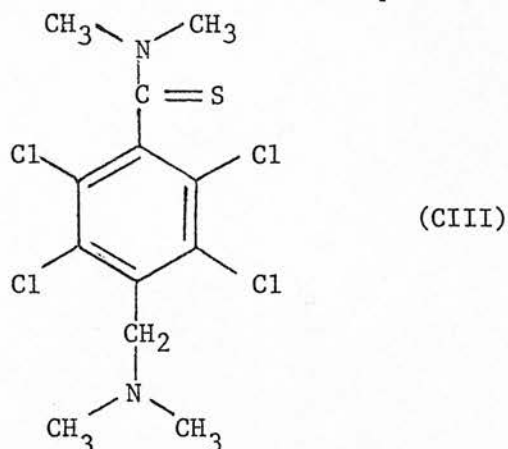
A possible compound corresponding to this molecular formula is the sulphenamide (CII) which could be visualised as being formed by interaction of dimethylamine (formed from dimethylformamide) with a cation (CI). The latter could be formed from the benzobis (dithiolethione) (C) and might have served as a direct precursor of the required sulphocarbon had it not been otherwise intercepted. (Scheme 11).

A second high-melting solid, dark brown in colour, was isolated and in this case the mass spectrum showed a parent ion peak at  $m/e$  360. The spectrum in the region of the parent ion conformed closely to the pattern expected for a 4 chlorine system. viz.



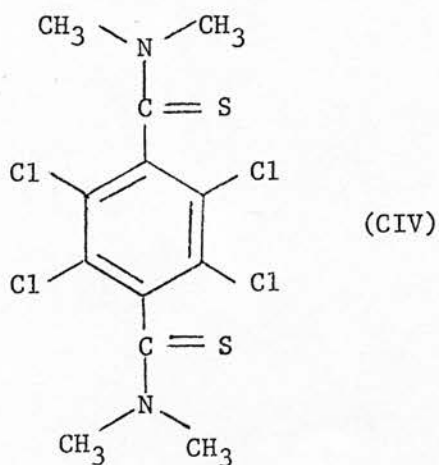
This information suggested the molecular formula to be  $\text{C}_{12}\text{H}_{14}\text{Cl}_4\text{N}_2\text{S}$  and this was verified by exact mass measurement. Substitution of this formula into a computer programme designed to calculate mass spectral isotope distributions produced a pattern identical with that obtained from the original sample.

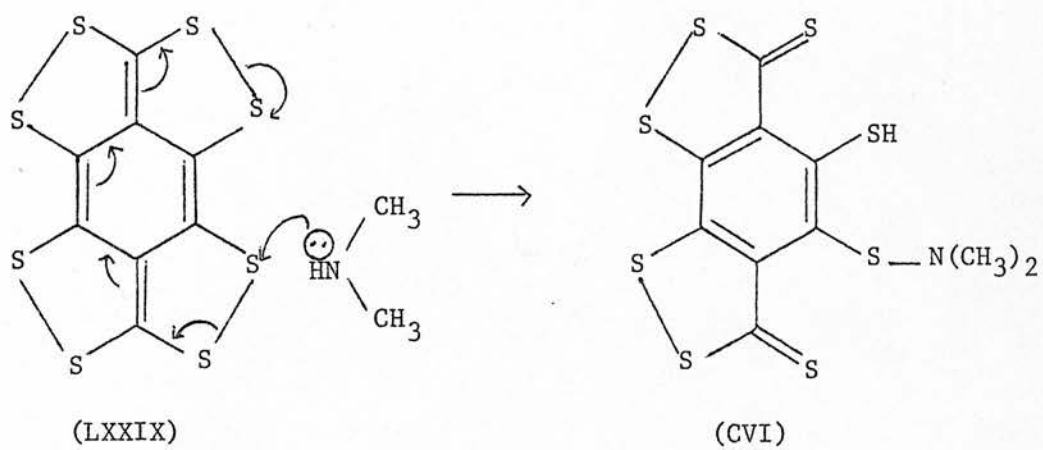
The thioamide (CIII) shown below is a possible structure



which could have been formed by attack of dimethylamine on the starting material, followed by dehydrogenation and sulphurisation to form the thioamide. The mass spectrum shows a P-44 peak, confirmed by a corresponding metastable ion peak, which could be formed by loss of  $\text{N}(\text{CH}_3)_2$ .

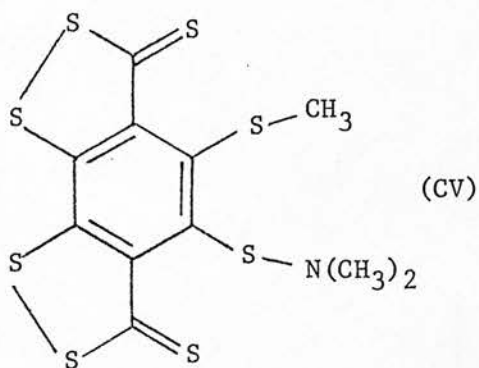
A third high melting solid, orange in colour, obtained in small quantity from chromatography was investigated by mass spectroscopy and the parent ion complex obtained was very similar to that obtained from the thioamide above. The peak of highest abundance occurred at  $m/e$  390 from  $3 \times {}^{35}\text{Cl}$  and  $1 \times {}^{37}\text{Cl}$  of the four chlorine pattern. It was thought possible that this compound might be of the following structure (CIV), being a further oxidised form of the thioamide (CIII). This compound would be expected





to be more polar than the thioamide (CIII) because of the added thione group.

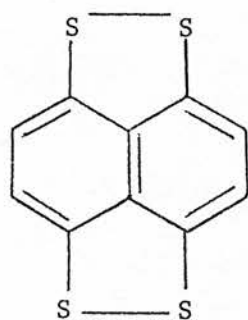
The fourth compound obtained by chromatography was brown in colour and its mass spectrum did not show any isotopic distribution consistent with the presence of chlorine in the molecule. The parent ion in this case occurred at  $m/e$  411, indicating an odd number of nitrogen atoms, and showed a  $p + 2$  peak of 35% consistent with the presence of eight sulphur atoms (sulphur isotope  $^{34}\text{S}$  occurs in a natural abundance of 4.2%). Exact mass measurement indicated an empirical formula  $\text{C}_{11}\text{H}_9\text{N S}_8$  which is consistent with the structure (CV).



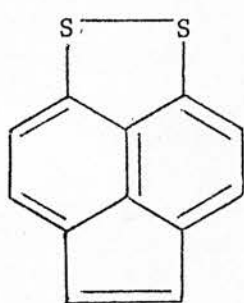
Postulation of this structure poses the question as to whether the desired sulphocarbon (LXXIX) had been formed and subsequently attacked by the solvent or aliphatic amine, formed as suggested earlier. It is however difficult to envisage a mechanism for methylation at the SH group (CVI).

2. Compounds Containing one or more 1,2-dithiole Rings Fused to a Naphthalene Nucleus

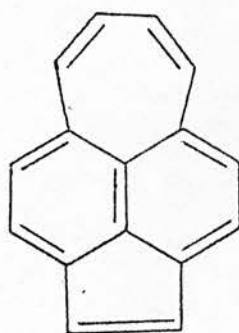
Among the many possible compounds within this general class, the naphthobis-1,2-dithiole (CVII) was of obvious interest in this investigation since it is closely related to "tetracene tetrasulphide" which is known to be electrically conducting.<sup>(45)</sup> The acenaphthylene derivative (CVIII) was also of interest (though unlikely to show appreciable conductivity) as a heterocyclic analogue of the hydrocarbon acepleiadylene (CIX). The latter compound has been shown to possess considerably more stability than pleiadylene (CX) which lacks the five membered ring, and this has been attributed to the presence of a  $14\pi$ -electron periphery in acepleiadylene.<sup>(76)</sup> Compound (CVIII) might be expected to be similarly stabilised with respect to naphtho [1,8-cd] [1,2]dithiole (CXI).



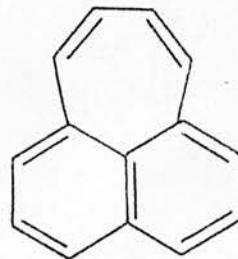
(CVII)



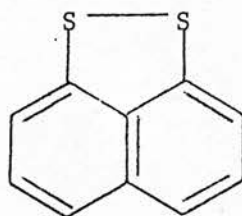
(CVIII)



(CIX)



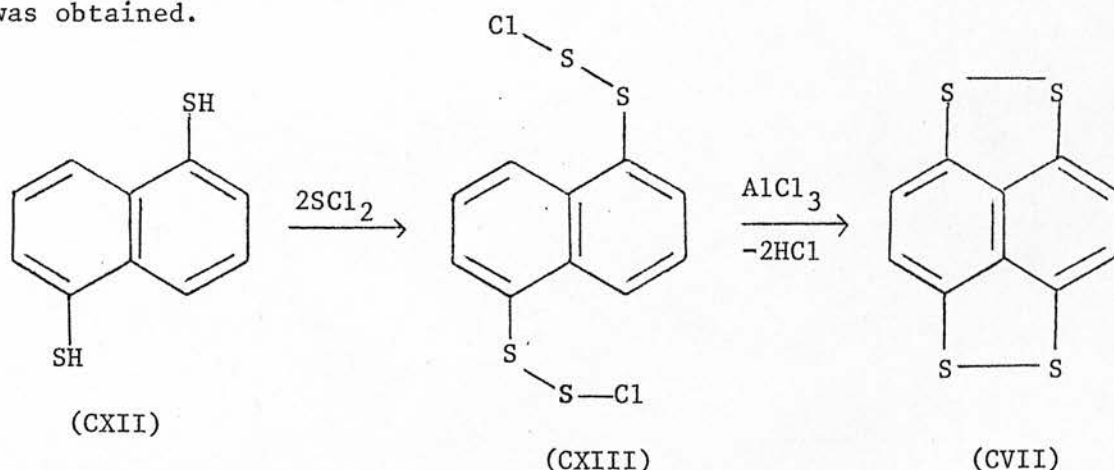
(CX)



(CXI)

(a) Attempted Synthesis of Naphtho[1,8-cd; 4,5-c<sup>1</sup>d<sup>1</sup>]bis[1,2]-dithiole.

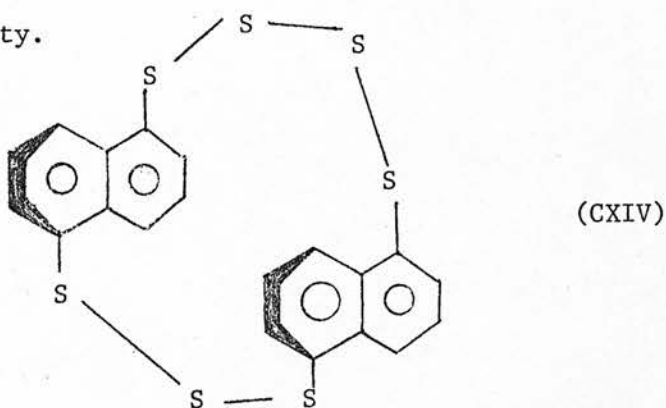
It has been reported<sup>(77)</sup> that benzenedithiols are converted into the respective bis(chlorodithio)benzenes by reaction with sulphur dichloride. An extension of this reaction into the naphthalene series, as shown below, starting from naphthalene-1,5-dithiol (CXII), was attempted and the crude product (CXIII) was treated with aluminium chloride. Starting material, sulphur, and chlorinated naphthalene derivatives were recovered but none of the desired naphtho[1,8-cd; 4,5-c<sup>1</sup>d<sup>1</sup>]bis[1,2]-dithiole (CVII) was obtained.



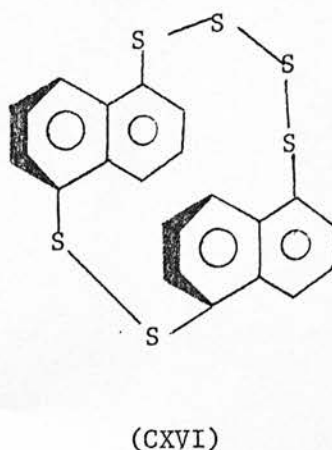
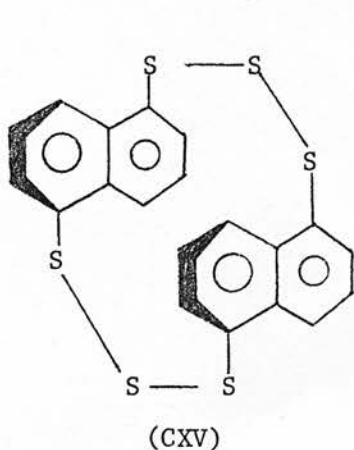
An alternative approach from naphthalene-1,5-dithiol was considered using thionyl chloride as the source of the two additional sulphur atoms. When these reactants were heated together, the reaction mixture quickly solidified. The yellow solid produced showed a singlet at  $\tau = 2.7$  in the p.m.r. spectrum and the mass spectrum (which was obtained at 260°C) showed peaks at  $m/e$  476:478 corresponding to a seven-sulphur system, and peaks of much greater

intensity at  $m/e$  444:446. Exact mass measurements on these peaks corresponded to formulae of  $C_{20}H_{12}S_7$  and  $C_{20}H_{12}S_6$ , respectively, which suggest the formation of a cyclophane-type system including two naphthalene nuclei with bridging sulphur atoms. The evidence is consistent with two possibilities of which the second seems the more likely in view of the greater abundance of the  $C_{20}H_{12}S_6$  ion.

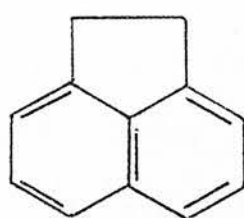
- 1) The compound  $C_{20}H_{12}S_7$  is the only product and that  $C_{20}H_{12}S_6$  is then a fragment ion formed by sulphur extrusion. The structure (CXIV) would then seem to be the most likely possibility.



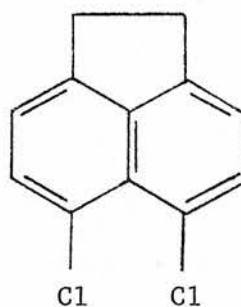
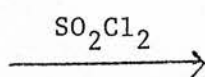
- 2) The material is a mixture of  $C_{20}H_{12}S_7$  and  $C_{20}H_{12}S_6$  as the main products. In this case  $C_{20}H_{12}S_7$  would be as above or an isomer thereof and  $C_{20}H_{12}S_6$  would be either a [4,2]-bridged system (CXVI) or a [3,3]-bridged system (CXV) as shown below.



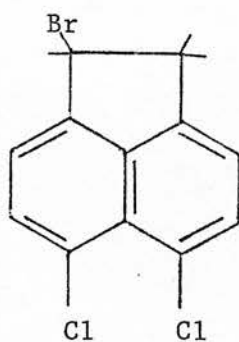
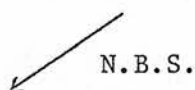




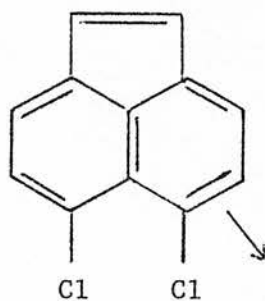
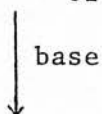
(CXVII)



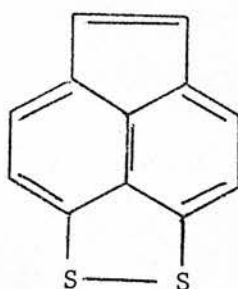
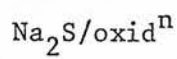
(CXVIII)



(CXIX)



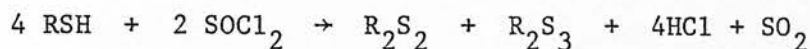
(CXX)



(CVIII)

Scheme 12

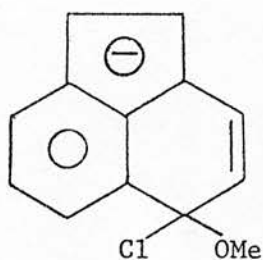
The [3,3]-bridged system seems the more likely possibility in view of previous reports<sup>(78)</sup> that thiols react with thionyl chloride according to the equation.



A molecular model suggests that such a structure would be relatively strain free.

(b) The Attempted Preparation of Acenaphtho[5,6-cd][1,2]-dithiole.

The proposed synthetic route to acenaphtho[5,6-cd][1,2]-dithiole (CVIII) starting from acenaphthene (CXVII) is shown opposite (Scheme 12). This route involves initial chlorination of acenaphthene in the 5-, and 6-positions, followed by bromination and subsequent dehydrobromination to introduce the ethylene bridge. Nucleophilic displacement of chlorine by sulphide (or hydrosulphide) ion was expected to occur fairly easily since 5-chloroacenaphthylene has been shown to be similarly substituted by methoxide ion,<sup>(79)</sup> a circumstance which may be attributed to the presence of a cyclopentadienide anion in the Wheland intermediate (CXXI). The dithiole ring would then be created in the final stage by oxidation.



(CXXI)

5,6-Dichloroacenaphthene (CXVIII) had previously been reported<sup>(80)</sup> as a further chlorination product of 5-chloroacenaphthene. The yield, however, was low and since the conversion of acenaphthene to 5-chloroacenaphthene and of the latter to 5,6-dichloroacenaphthene were both effected with sulphuryl chloride it seemed possible that a better yield might be obtained by allowing the reaction to proceed directly from acenaphthene without isolation of the intermediate monochloro-compound.

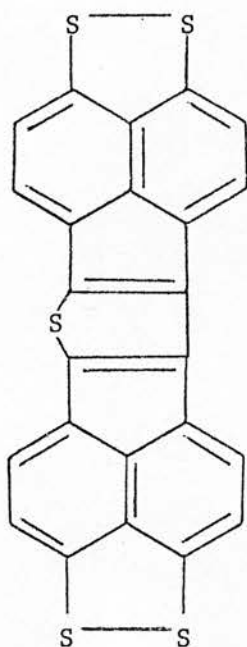
The reaction was allowed to proceed for five days but gave only a low yield (6%) of 5,6-dichloroacenaphthene. Addition of anhydrous ferric chloride<sup>(81)</sup> to the reaction mixture increased the yield of product to 36% after two days but the product was dark in colour and required a tedious purification by Soxhlet extraction. When anhydrous aluminium chloride was used as the catalyst the reaction mixture solidified after only 30 minutes and gave pure 5,6-dichloroacenaphthene in 65% yield.

The conversion of the acenaphthene nucleus to the corresponding acenaphthylene (CXX) was accomplished by the standard bromination-dehydrobromination method. Bromination with N-bromosuccinimide in the presence of benzoyl peroxide gave 1-bromo-5,6-dichloro-acenaphthene (CXIX) in moderate yield. Dehydrobromination was achieved by heating with 2,4,6-collidine or N,N-diisopropylethylamine, to give 5,6-dichloroacenaphthylene as yellow plates, the second reagent giving the better yield.

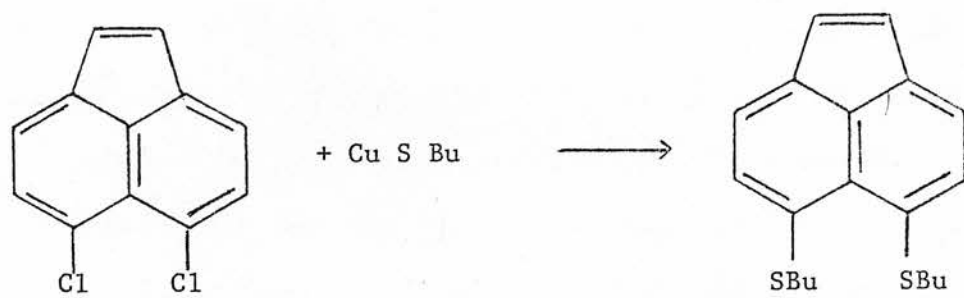
In an attempt to obtain the dithiol (CVIII), the dichloro-acenaphthylene was heated with sodium sulphide nonahydrate in

dimethylformamide. Work up of the reaction mixture led to recovery of impure starting material, the mass spectrum of which showed a very weak peak at the  $m/e$  value expected (214) for the required disulphide (CVIII). However, this product was present only in trace quantities and on further slow heating of the sample in the mass spectrometer, the 214 peak disappeared. The use of anhydrous sodium sulphide in place of the nonahydrate gave similar results but an insoluble compound of higher molecular weight ( $m/e$  456) was also produced.

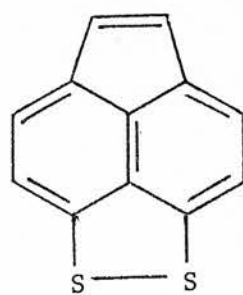
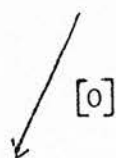
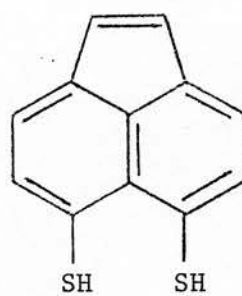
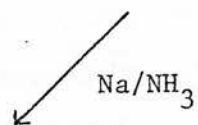
This parent ion peak also contained a  $p + 2$  peak of 20% (which corresponds to a 5 sulphur system) and suggests a molecular formula of  $C_{24}H_8S_5$ . A possible structure is shown below (CXXII) and this ring system lacking the S-S bridges, is known as a product of fusion of acenaphthene with sulphur.<sup>(82)</sup>



(CXXII)



(CXX)



(CVIII)

Scheme 13

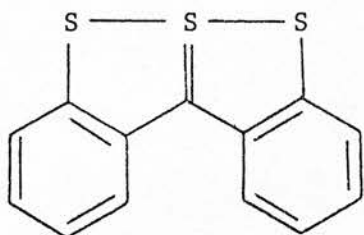
Another approach was planned based on a general method for the synthesis of arenethiols<sup>(77)</sup> using cuprous n-butyl mercaptide and aryl bromides with subsequent reductive dealkylation in liquid ammonia (Scheme 13). Although aryl chlorides are reported not to react with cuprous n-butyl mercaptide,<sup>(83)</sup> the proposed reaction was considered feasible because of the activating effect of the 5-membered ring in promoting nucleophilic attack at the 5- and 6-positions of acenaphthylenes.

Again, however, the attempted nucleophilic displacement yielded largely starting materials together with an unidentified product.

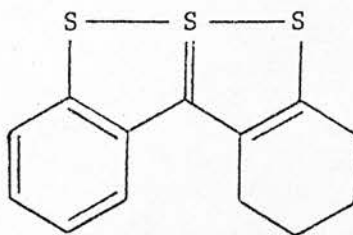
3. Compounds Containing Thiathiophthen Ring Systems Fused to an Anthracene or to a Thioxanthene Nucleus

One important feature which has emerged from the numerous X-ray diffraction studies of thiathiophthens is the similarity of the geometry of the five-carbon system to that present in one half of the naphthalene molecule.<sup>(13)</sup> It follows that fusion of benzene rings to the 2,3- and 4,5-bonds is not likely to perturb the thiathiophthen system appreciably and it is reasonable to suppose that the resulting compounds should be stable.

A search of the literature shows that, though a few monobenzothiathiophthens<sup>(84)</sup> e.g. [(CXXIII)] are known, the dibenzo-derivative (CXXIV) is not. Klingsberg has shown, moreover, that the tetrahydrodibenzo-compound (CXXIII) cannot be dehydrogenated by heating with sulphur.<sup>(85)</sup>



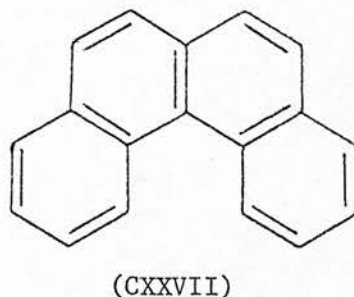
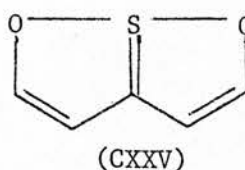
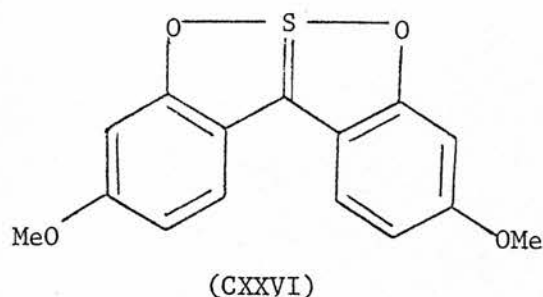
(CXXIV)



(CXXIII)

In contrast to this situation, the 1,6-dioxa-6a-thiapentalene<sup>(86)</sup> system (CXXV) was first observed to exist as a dibenzo-derivative (CXXVI); compounds lacking the fused benzene rings were prepared more recently by Reid and his coworkers.<sup>(87)</sup>





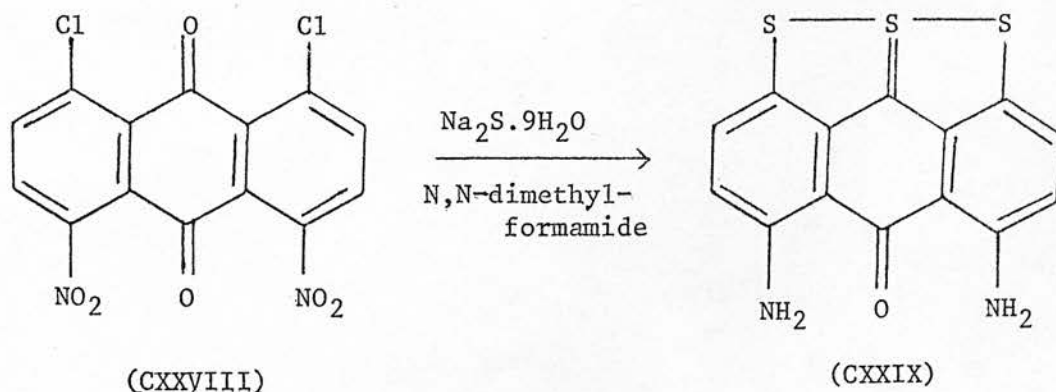
It is possible that the difficulties encountered in the preparation of dibenzothiathio-phthens might be associated with steric interference of hydrogen atoms on adjacent carbon atoms of the two benzo-rings. The extent of interference would be similar to that found in benzo[C]phenanthrene (CXXVII) but, in contrast to the situation in the latter compound, any deviation from coplanarity that the system might adopt, in order to relieve the overcrowding, might at the same time so disturb the rather delicate bonding situation in the trisulphur system that instability would be introduced. X-ray diffraction<sup>(88)</sup> shows that in the dioxo-analogue, which has shorter O-S in place of S-S bonds, the two benzo-rings are pulled apart so that the critical H-H distance, while still quite short ( $2.02\text{\AA}$ ), is sufficiently great to allow the system to remain planar to within  $0.06\text{\AA}$ . An obvious way in which to overcome the possible steric problem in dibenzothiathio-phthen is to connect the two benzo-rings by a one-atom bridge.

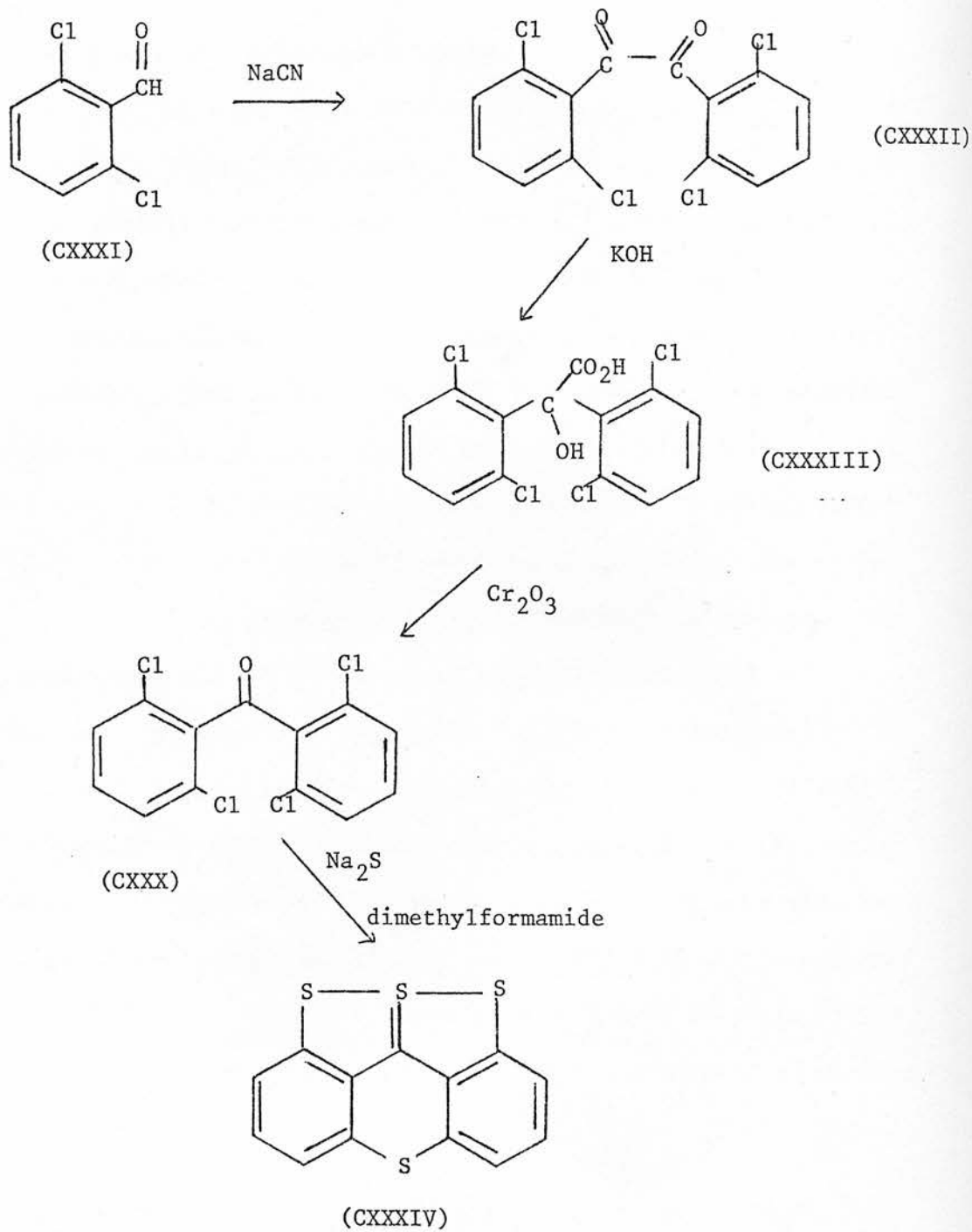


The first example of a bridged dibenzothiathiophthen was Davidson's anthrone derivative (LVII) which was synthesised in one stage by the reaction of 1,8-dichloroanthraquinone (LVI) with sodium sulphide. (29) The mechanism of this reaction is somewhat obscure but is clearly dependent on the ease of nucleophilic displacement of chlorine in the  $\alpha$ -position of anthraquinone. Extension of the reaction to 1,4,5,8-tetrachloroanthraquinone gave the anthrabis(thiathiophthen) (LXa). The object of the present investigation was to further characterise Davidson's compounds and to synthesise additional examples of the same type.

(a) Synthesis of Bridged Dibenzothiathiophthens.

The first reaction to be investigated was a simple extension of Davidson's work in which 1,8-dichloro-4,5-dinitroanthraquinone (CXXVIII) was treated with sodium sulphide in boiling dimethyl-formamide. It was expected that the nitro-groups would render the chlorine atoms even more susceptible to nucleophilic displacement and gratifying to find that the reaction proceeded rapidly to give a good yield of a deep green product.





Scheme 14

Unlike Davidson's anthrone derivative this compound was relatively easily purified by recrystallisation. Elemental analysis, mass spectroscopy, and infra-red spectroscopy showed however, that the product was the diamine (CXXIX). The sodium sulphide had caused reduction of the nitro groups, this being a well-known method for the preparation of aromatic amines,<sup>(89)</sup> particularly in the anthraquinone series.

Another type of bridging atom or group which might be used to stabilise the dibenzo-thiathiophthen system is a heteroatom such as O, S, or N-alkyl. A simple but low yield synthesis of the sulphur-bridged compound is shown in Scheme 14.

This route involves the treatment of 2,2',6,6'-tetrachlorobenzophenone (CXXX) with sodium sulphide in boiling dimethylformamide. The 2,2',6,6'-tetrachlorobenzophenone was obtained by a conventional reaction sequence from 2,6-dichlorobenzaldehyde (CXXXI) by benzoin condensation, benzilic acid rearrangement, and chromium trioxide oxidation. The benzoin condensation, like that of certain other hindered benzaldehydes,<sup>(90)</sup> yields the benzil directly, thus conveniently shortening the planned sequence by one oxidation stage.

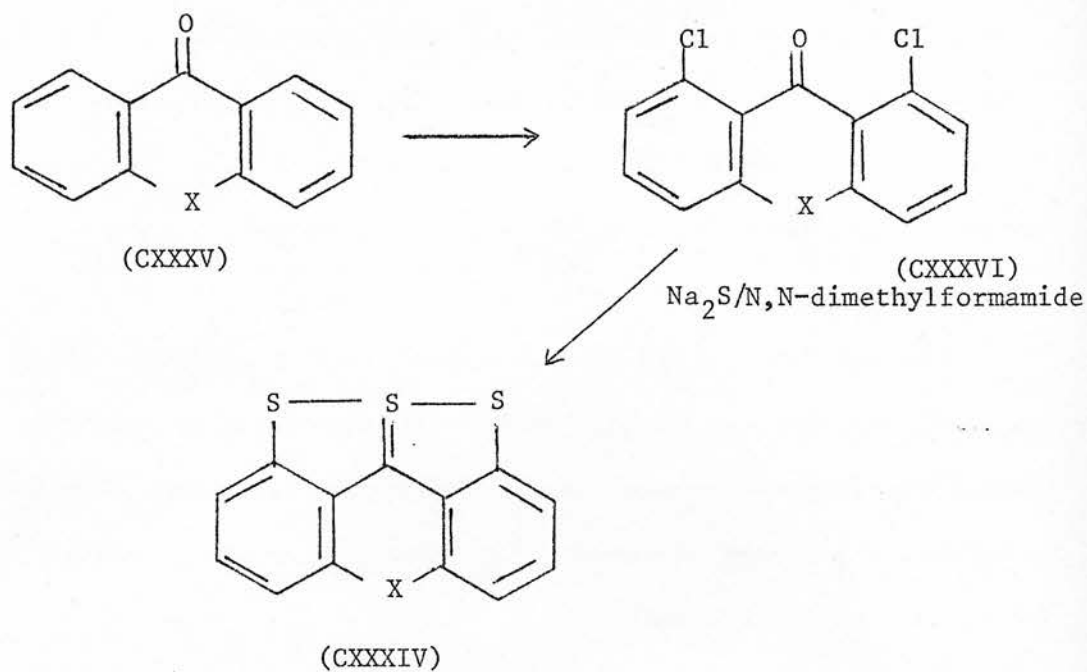
The benzil (CXXXII) was obtained in moderate yield as an easily crystallisable yellow solid with a carbonyl absorption in the i.r. at  $1715\text{ cm}^{-1}$ . The p.m.r. showed only one singlet in the aromatic region as expected while the mass spectrum produced no molecular ion for the parent compound owing to the facile scission of the carbonyl-carbonyl bond.

The benzilic acid rearrangement produced a high yield of product (XXXIII) which showed the expected carbonyl and hydroxyl absorptions in the i.r. at  $1700\text{ cm}^{-1}$  ( $\text{C=O}$ ) and at  $3290\text{ cm}^{-1}$  ( $\text{-OH}$ ). A broad peak in the p.m.r. spectrum at low  $\tau$  value indicated the presence of  $\text{-OH}$  and  $\text{CO}_2\text{H}$  groups and again the mass spectrum showed a weak molecular ion, the major fragmentation being decarboxylation.

The oxidation stage with chromium trioxide produced a high yield of well-defined colourless crystals whose p.m.r. spectrum showed the expected aromatic singlet. The mass spectrum showed a molecular ion peak of correct  $m/e$  value, the major fragmentation being loss of an aryl radical.

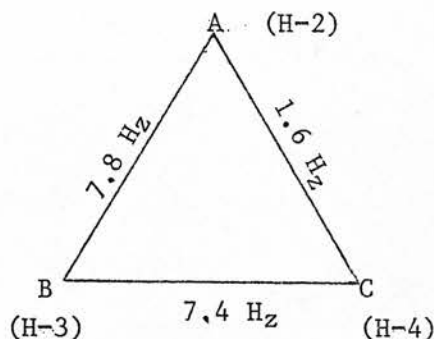
The conversion of 2,2',6,6'-tetrachlorobenzophenone (CXXX) to the "trithio-thioxanthene" (CXXXIV) by treatment with sodium sulphide in boiling dimethylformamide was a low yield step (16%). The desired compound was separated by chromatography from an unidentified yellowish green solid from which further small amounts of the required compound could be obtained by extraction and/or sublimation.

The "trithio-thioxanthene" (CXXXIV) was a sparingly soluble compound forming deep purple plates. Analysis and mass spectrometry confirmed the molecular formula and the  $^1\text{H}$  n.m.r. spectrum, which had to be obtained by Pulsed Fourier Transform because of low solubility, showed an essentially first-order splitting pattern (AMX) due to three adjacent protons on each of the two equivalent benzenoid rings.



- X = -CO (a)  
 -S (b)  
 -O (c)  
 -N - alkyl (d)  
 -CH<sub>2</sub> (e)

SCHEME 15



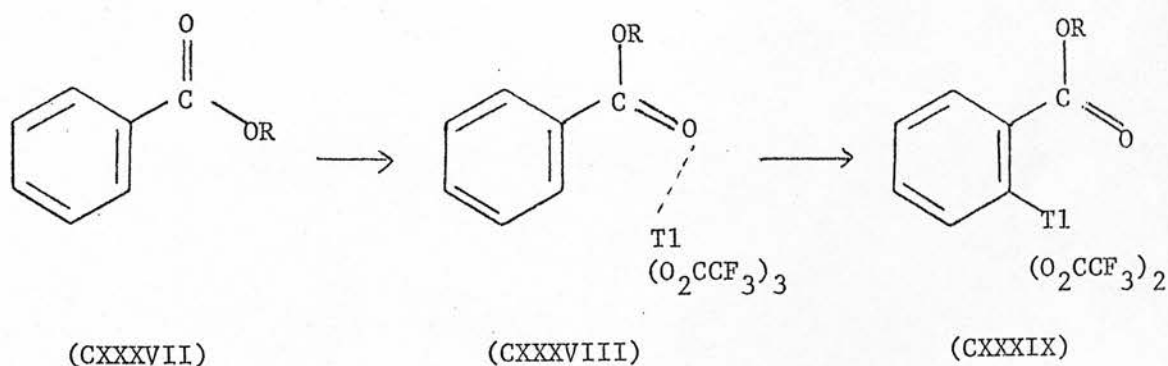
The electronic spectrum showed 5 maxima, the one corresponding to the lowest energy transition being at 540 nm. This represents a considerable hypsochromic shift with respect to the corresponding maximum in the "trithioanthrone" which occurs at 620 nm.

Since the synthetic route outlined above is specific to the sulphur-bridged compound, a more general synthetic scheme was required in order to extend the range of bridging groups. In view of the ready conversion of 1,8-dichloroanthraquinone with sodium sulphide into the corresponding "trithio-anthrone", the introduction of halogen substituents into the 1- and 8-positions of xanthone (CXXXVc), acridone (CXXXVd), or anthrone (CXXXVe), seemed likely to be a worthwhile primary objective in the development of such a general scheme.

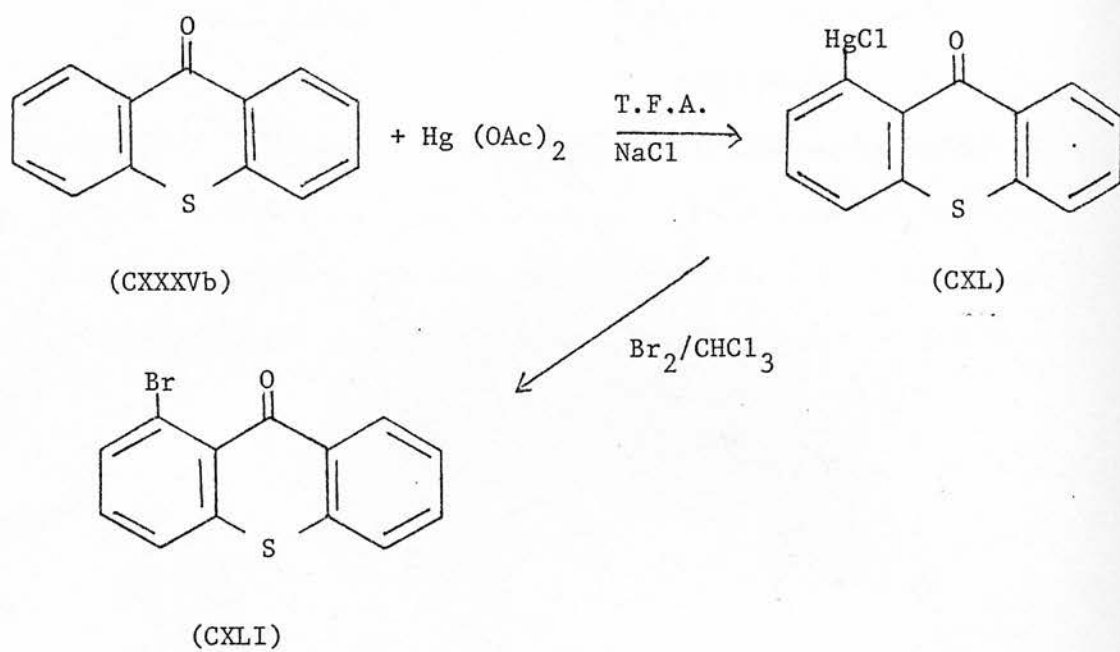
Conventional halogenation of a compound of general structure (CXXXV) causes substitution at the 2- or 4-position of the ring owing to the meta-directing effect of the carbonyl group. A reagent was therefore required to specifically substitute the 1-position and which could then be directly displaced to form the desired 1-halogeno compound. This treatment could then be repeated on the other ring to afford the 1,8-dihalogeno-product. In searching for such a regio-specific reagent, thioxanthone (CXXXVb)

was used as a substrate because the end-product (CXXXIV) of the synthesis was now a known compound, having been synthesised by the route discussed previously, and its formation could thus serve as a check on the success of the initial 1,8-disubstitution.

A recently reported electrophilic substitution which occurs ortho to a carbonyl group is the reaction of benzoate esters (CXXXVII) with thallium (III) trifluoroacetate.<sup>(91)</sup> The authors suggest that the thallium salt first forms a complex (CXXXVIII) with the carbonyl oxygen and that this facilitates delivery of the thallium to the ortho-position of the benzene ring (CXXXIX).



It seemed possible that the application of this reaction to thioxanthone, and subsequent reaction with potassium iodide might produce 1-iodothioxanthone. The reaction was carried out using trifluoroacetic acid as solvent and later acetonitrile. No attempt was made to isolate the organothallium compound but the reaction mixture was treated directly with potassium iodide. Thioxanthone and thallium (I) iodide were recovered but no 1-iodothioxanthone was formed.

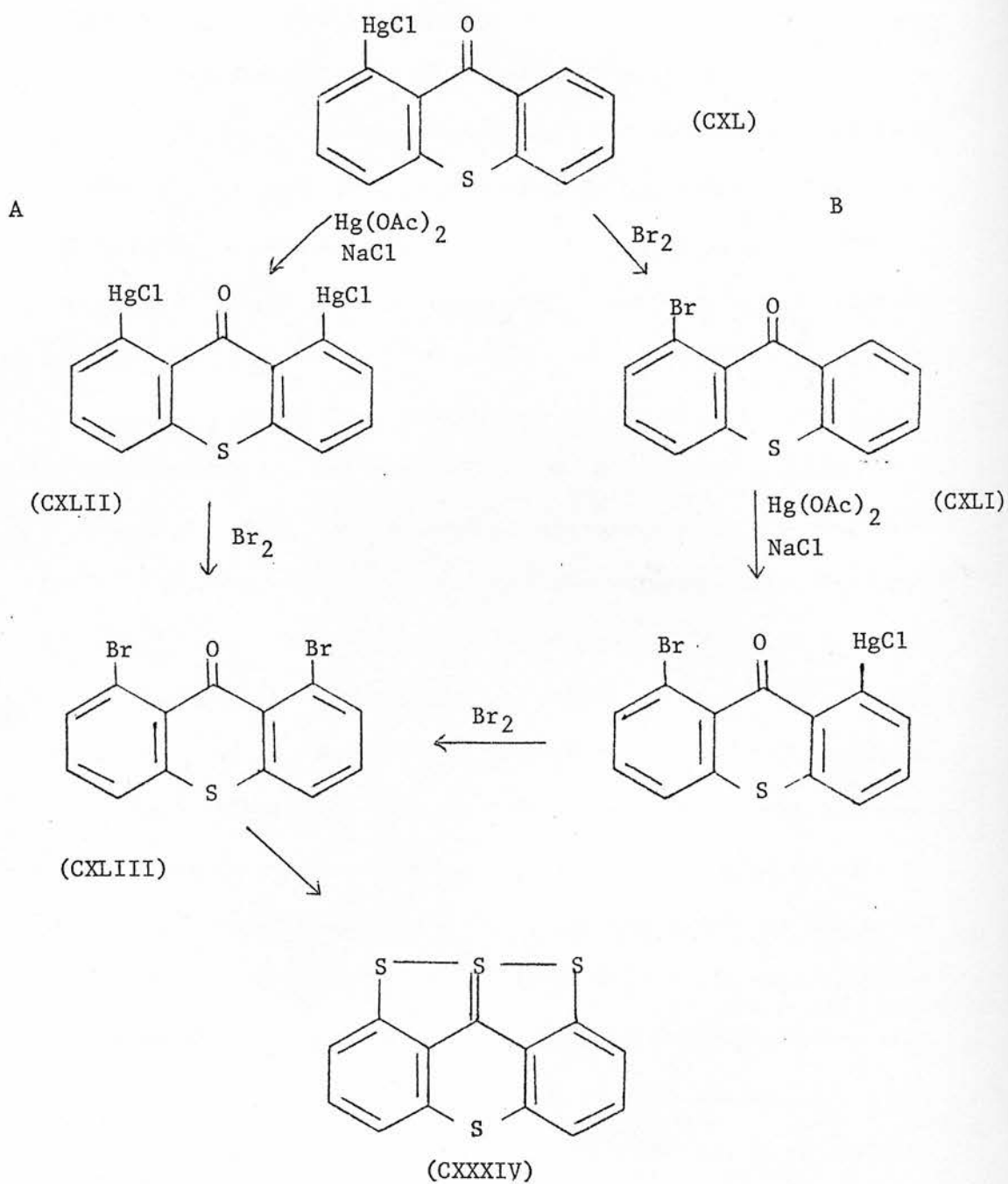




Another type of electrophilic substitution which may occur ortho to an electron-withdrawing group is mercuration. Examples of such reactions have been known for much longer than the analogous thallation reactions and one noteworthy application is the mercury-catalysed sulphonation of anthraquinone (CXXXVa) to give the  $\alpha$ -sulphonic acid rather than the  $\beta$ -isomer which is obtained in the absence of mercuric ion. The reaction is believed<sup>(92)</sup> to occur by initial mercuration (via a carbonyl -  $\text{Hg}^{++}$  complex) followed by displacement of mercury by a sulphonic acid group.

Mercuration<sup>(93)</sup> in most other cases is usually carried out by treatment of the substrate with mercury (II) acetate and the resulting acetoxymercuri-derivative is then treated with sodium chloride to give the less soluble chloromercuri-derivative. Application of this reaction to thioxanthone (CXXXVb) produced a compound which was shown by mass spectrometry to be a monochloromercurithioxanthone (CXL). The compound was insufficiently soluble to allow a p.m.r. spectrum to be readily obtained and so at this point the structure was assumed to be 1-monochloromercurithioxanthone (CXL). The reaction was carried out in trifluoroacetic acid a solvent which is known to increase the rate of mercuration.<sup>(94)</sup> The use of acetic acid as solvent produced no reaction. The repetition of the above reaction on xanthone (CXXXVc, X = O) produced similar results.

As shown in scheme 16 (route B) bromine was allowed to react on the 1-monochloromercurithioxanthone (CXL) producing a red solid. This was shown by t.l.c. to be a mixture but after column



SCHEME 16

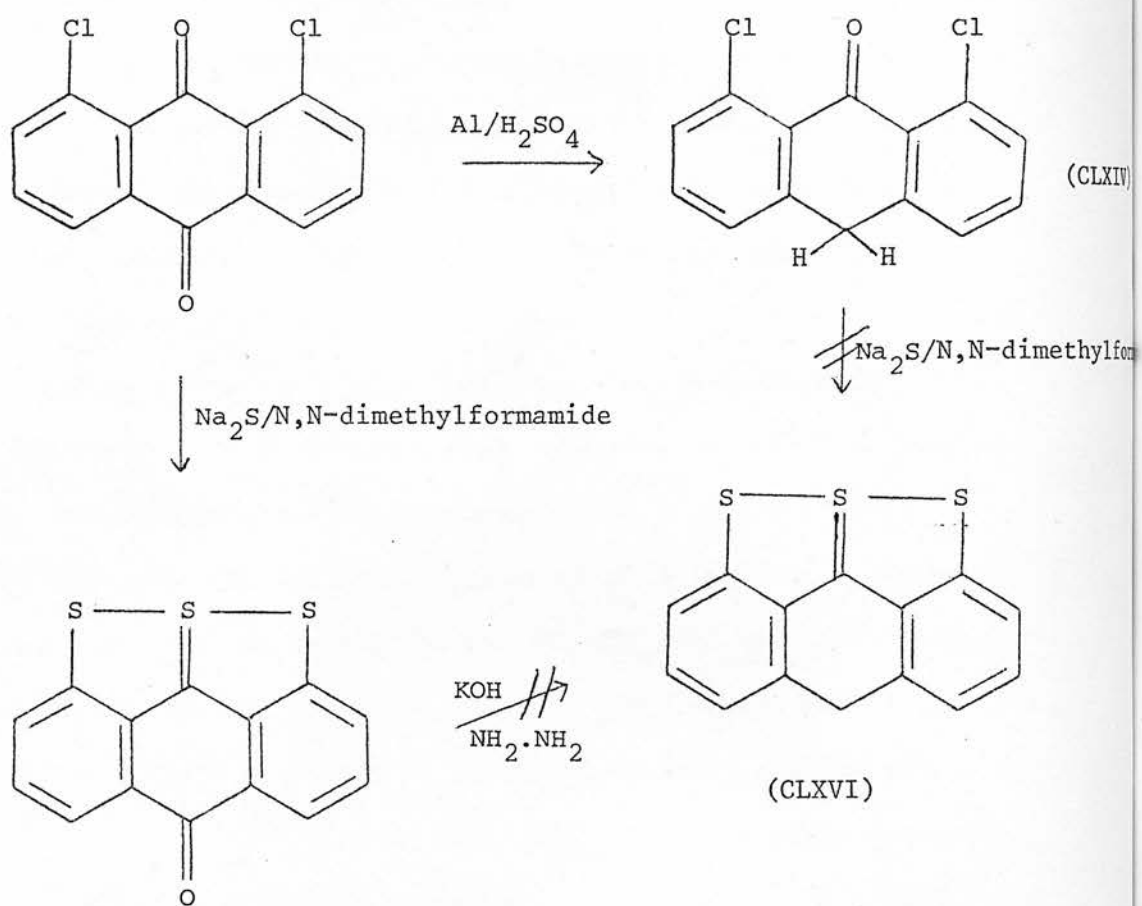
chromatography a purified product was obtained. Mass spectroscopy however, showed the product, 1-bromothioxanthone (CXLI), to be contaminated with a dibromothioxanthone impurity (the p.m.r. suggests this to be 1,7-dibromothioxanthone) but following further repeated chromatography pure 1-bromothioxanthone (CXLI) was obtained. The substitution was determined from the p.m.r. spectrum which showed 1 low field proton (1.4 $\tau$ ) and 6 higher field protons (2.3 $\tau$ ). Since this product showed substitution in the 1-position then the initial mercuriation would also have occurred at the 1-position.

Further reaction of the monochloromercurithioxanthone (CXL) [Scheme 16, route A] with mercuric acetate did not form the disubstituted compound (CXLII) and an attempt to form this compound directly from thioxanthone (CXXXVb) using two equivalents of mercuric acetate resulted merely in an increased yield of monochloromercurithioxanthone (CXL) (66% to 94%).

Because of secondary substitution occurring in route B of Scheme 16 and the great difficulty obtained in separating pure 1-bromothioxanthone it was apparent that these were not viable routes to 1,8-dibromothioxanthone (CXLII).

The synthesis of a dibenzothiathiofthen containing the methylene bridge ( $X = CH_2$ ) was now considered and two routes from 1,8-dichloroanthraquinone (LVI) were investigated (Scheme 17).

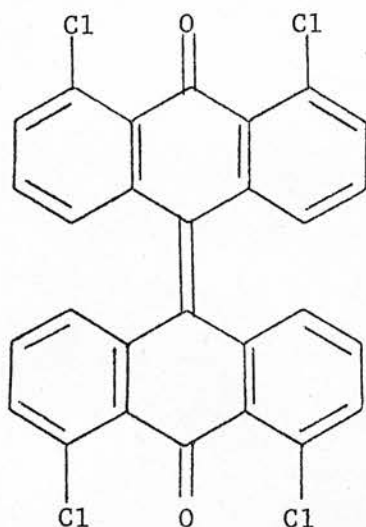
1,8-Dichloroanthraquinone was reduced to the 1,8-dichloroanthrone (CXLIV) by aluminium and concentrated sulphuric acid. The carefully purified product was then treated with sodium sulphide in dimethylformamide but the product which was obtained, along with starting material, was the oxidation product 1,8-dichloroanthraquinone. When



SCHEME 17

ethanol was employed as solvent, the reaction mixture immediately turned red on addition of sodium sulphide and deposited a solid, the i.r. spectrum of which showed a carbonyl absorption ( $\nu = 1690 \text{ cm}^{-1}$ ). The mass spectrum indicated a parent ion at  $m/e$  522 which showed a four-chlorine pattern and suggested the formation of the dianthrone<sup>(95)</sup> (CXLV) by oxidative dimerisation.

In view of the well known applications of sodium sulphide as a reducing agent, oxidation of the anthrone in these experiments seems anomalous though it is not inconsistent with the formation of the fused thiathiophthens, which also involves an oxidation step under the same conditions.

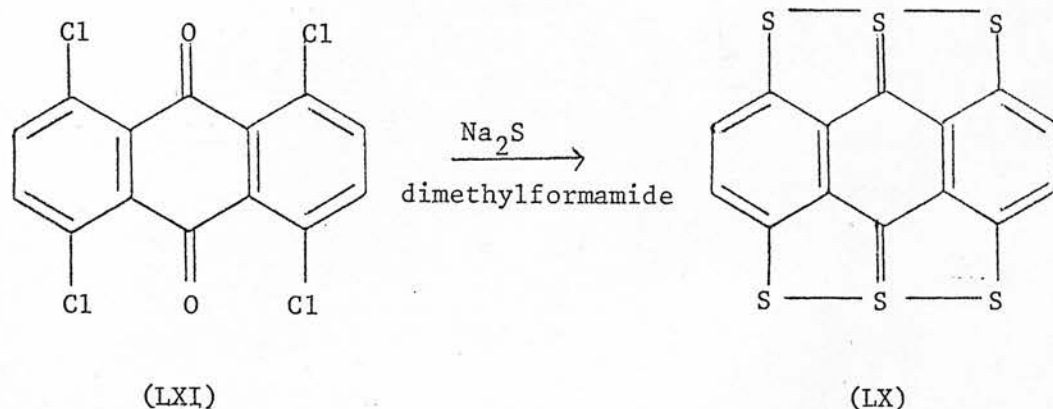


(CXLV)

As an alternative approach to the methylene-bridged dibenzothiathiophthens (CXLVI), an attempt was made to reduce the carbonyl group of the "trithioanthrone" using the Huang-Minlon<sup>(96)</sup> modification of the Wolff-Kischner reduction but only starting material was isolated from the reaction mixture.

b) Characterisation and Reactions of Anthra(1,9,8-bcde:5,10,4-b'c'd'e')bis(thiathiophthen)

1,4,5,8-Tetrachloroanthraquinone (LXI) has been shown by Davidson (see introduction) to react with sodium sulphide in boiling dimethylformamide to form "hexathioanthracene" (LX) as a

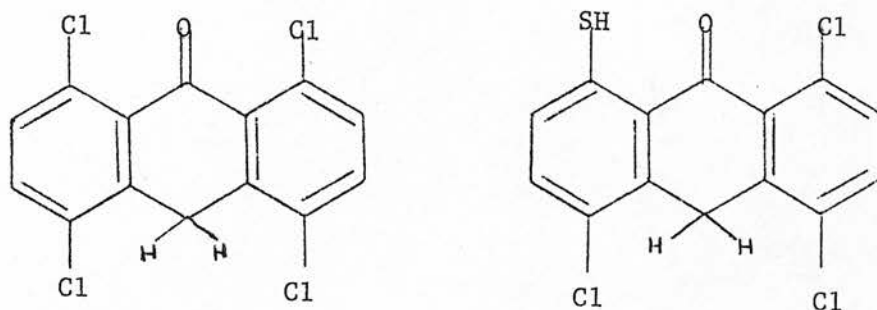


green microcrystalline solid, almost insoluble in all common solvents. Davidson did not obtain the "hexathioanthracene" analytically pure but inferred the formula (and structure) from exact mass measurements which gave it as  $\text{C}_{14}\text{H}_4\text{S}_6$ .

In order to obtain an analytically pure sample the starting materials and solvent were carefully purified and the product was purified by Soxhlet extraction first with dimethylformamide, then with 1,2,4-trichlorobenzene and finally with acetone. The residue in the thimble was the required product (LX) analytically pure.

In view of the low yield (15%) it was decided to investigate the dimethylformamide mother liquors and acidification produced a black solid. The mass spectrum of this material showed a four-chlorine pattern as the parent ion ( $m/e$  330 for  $^{35}\text{Cl}_4$ ) but there was a significant peak at  $m/e$  328 which was unlikely to be a

fragment ion peak. Exact mass measurements on these two peaks indicated the molecular formulae to be  $C_{14}H_6OCl_4$  and  $C_{14}H_7OSCl_3$  respectively. Possible structures consistent with these formulae are shown below.

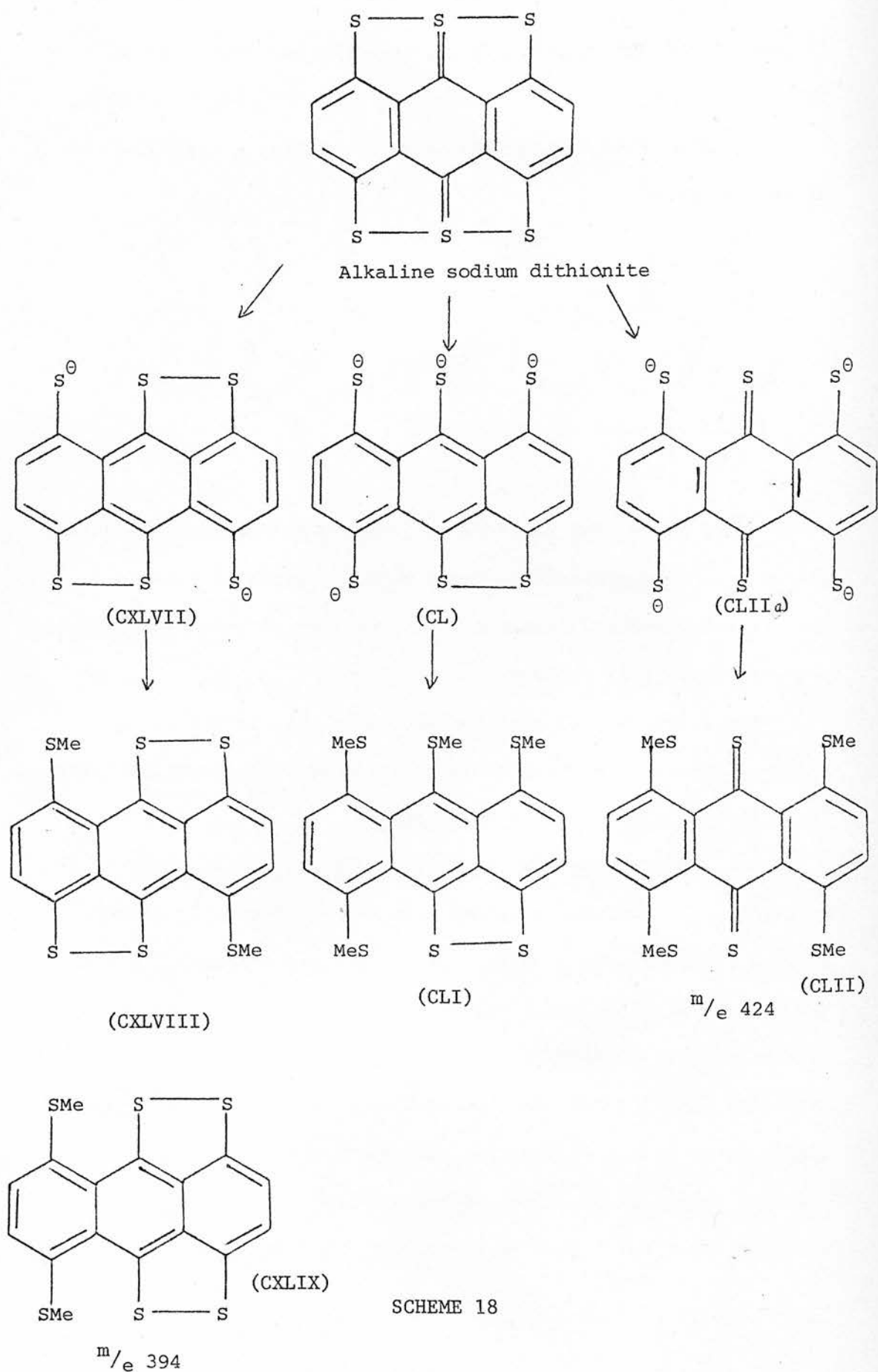


Since it was not possible to investigate "hexathioanthracene" directly by spectroscopic or X-ray methods, proof of structure must rest on chemical reactions which convert it into more soluble and characterisable products.

Two approaches to this end were used: (a) reduction by sodium dithionite followed by methylation and (b) direct methylation.

(a) Reduction Followed by Methylation

Despite the very low solubility of hexathioanthracene in all available solvents, the compound reacted fairly readily with aqueous alkaline sodium dithionite to form a homogeneous solution. The process of dissolution was accompanied by various colour changes attributable to progressive reduction of the disulphide linkages. The final solution obtained by reaction of the hexathioanthracene with a large excess of alkaline sodium dithionite was stirred with dimethyl sulphate and, after 24 hours at room temperature a solid had been deposited. This substance was found to be a mixture



SCHEME 18

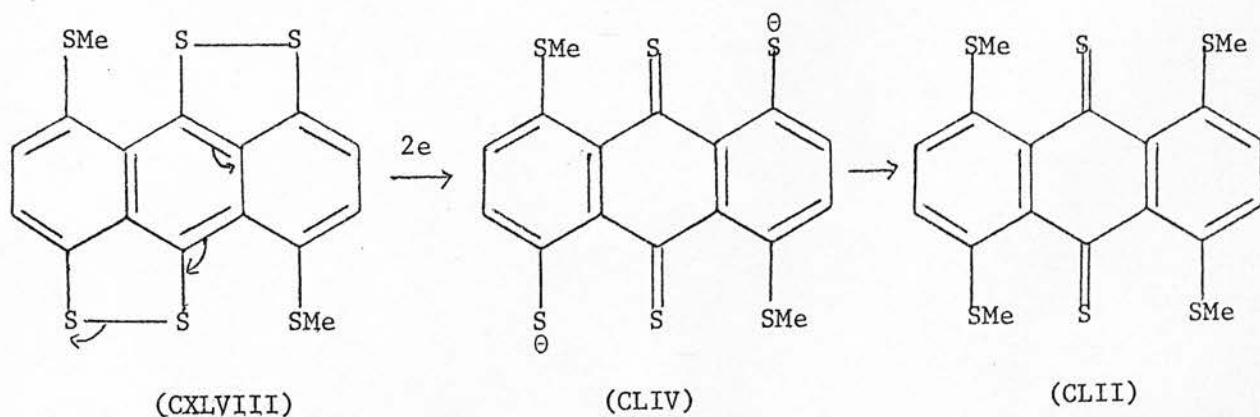


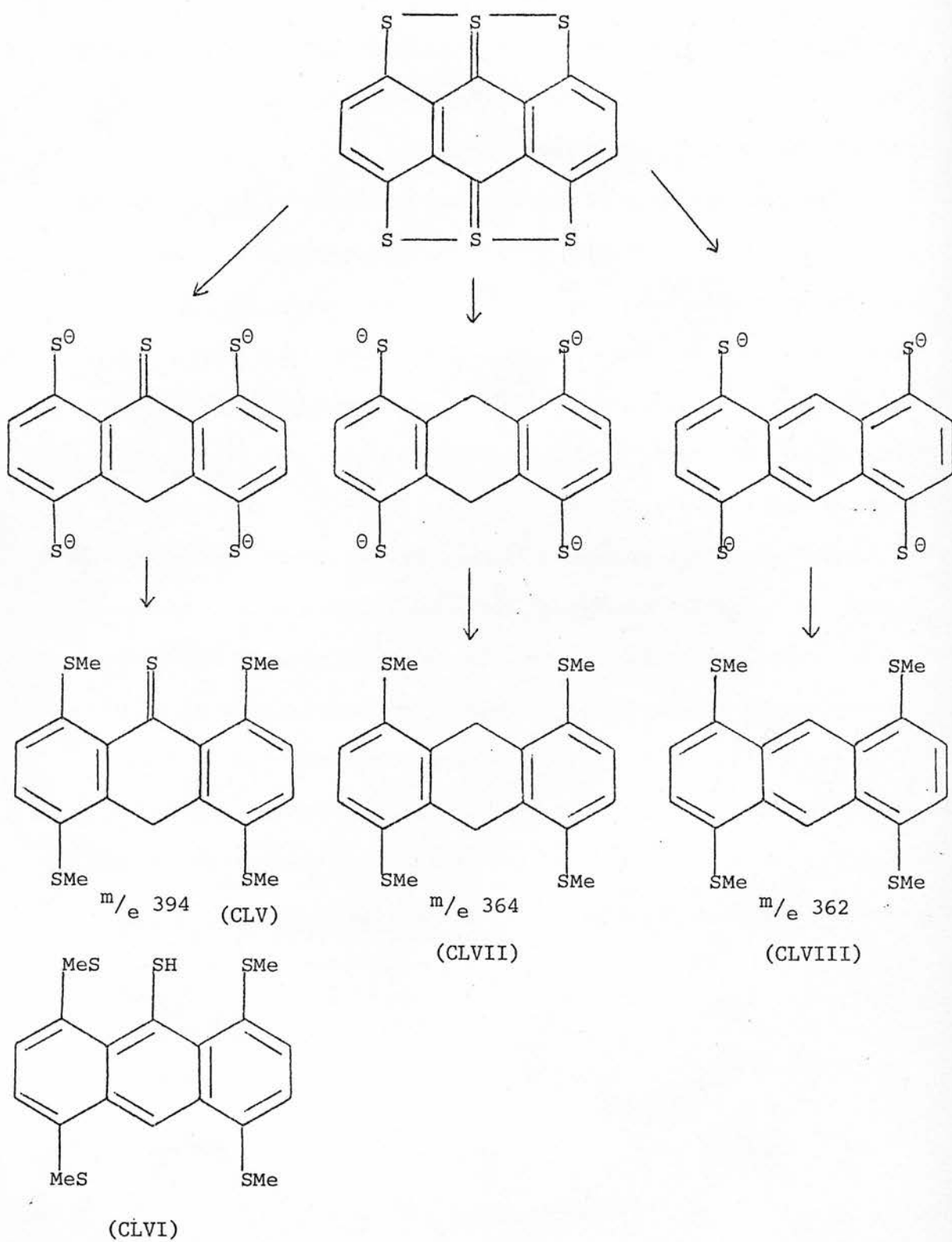
containing both chloroform-soluble and chloroform-insoluble products but the amount of each was small and their mass spectra suggested that neither product was a pure compound.

The mass spectrum of the chloroform-soluble component showed a parent ion peak at  $m/e$  394 (cf. hexathioanthracene  $M = 364$ ) together with prominent peaks at  $m/e$  379 and 364, presumably caused by successive loss of two methyl groups. A compound having the structure (CXLVIII) or (CXLIX) opposite possibly formed by methylation of a dianion such as (CXLVII) would be expected to produce such a mass spectrum.

The chloroform-insoluble product gave a parent ion at  $m/e$  424 though, being of low intensity, this could have been due merely to a minor component of the mixture. A molecular weight of this value corresponds to a tetramethyl derivative of hexathioanthracene (CLI) or (CLII) and suggests either (a) further reduction of the hexathioanthracene by the sodium dithionite to a tetrathiolate anion (CL) or (CLIIa) followed by methylation, or (b) reduction of the dimethyl hexathioanthracene followed by methylation as exemplified below.

(b)





SCHEME 19

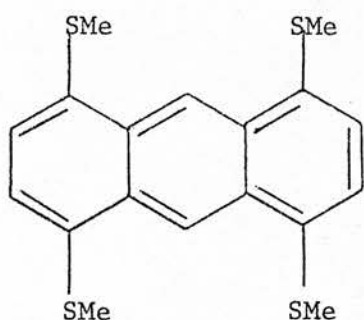
Other peaks in the spectrum could have been due to other components of the mixture and/or to fragment ions but, since insufficient material was available for purification, no reliable evidence could be obtained.

In an attempt to increase the yield of products, the reduction of hexathioanthracene was repeated and the solution was heated under reflux with dimethyl sulphate. A solid was deposited and this was again found to consist of both chloroform-soluble and chloroform-insoluble components.

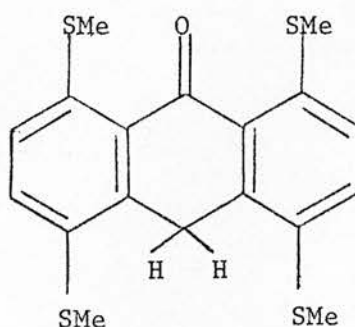
Thin layer chromatography of the chloroform solution ... indicated the presence of one pink and one yellow spot sufficiently different in retention times and apparently in sufficient quantity to warrant separation by column chromatography. The first product from the column gave an intensely crimson solution and its mass spectrum once again showed a parent ion peak at  $m/e$  394. Inspection of the fragmentation however showed successive losses of four methyl groups in marked contrast to the behaviour of the compound previously obtained. An exact mass measurement for the peak at  $m/e$  394 confirmed that it was not due to the dimethyl compound (CXLVIII) and indicated a molecular formula  $C_{18}H_{18}S_5$ , among the possible structures for which are the thioanthrone (CLV) and the tautomeric anthracenethiol (CLVI). Although such a structure could not fragment to give hexathioanthracene ( $m/e$  364) the mass spectrum did, in fact, show a significant peak at  $m/e$  364 and it seemed likely that this was due to another component of the mixture. An exact mass measurement for this peak indicated the molecular

formula  $C_{18}H_{20}S_4$  for which the structure (CLVII) is proposed (Scheme 19).

The second product from the column gave an intensely yellow solution which yielded a small quantity of yellow solid. Once again the mass spectrum was obtained and the parent ion occurred at  $m/e$  362 with an extremely small, higher mass peak at  $m/e$  378. The spectrum was identical with that of the "chloroform-insoluble" product obtained from the same reaction. In view of the presence of fragment ion peaks corresponding to four successive losses of methyl groups from the  $m/e$  362 peak it seemed likely that the main component of the mixture was 1,4,5,8-tetra(methylthio)anthracene (CLVIII). Exact mass measurement confirmed the molecular formula as  $C_{18}H_{18}S_4$  thus lending support to this conclusion. It seems likely that the peak at  $m/e$  378 was due to a trace of the corresponding anthrone (CLIX) which could have been formed by hydrolysis of the thioanthrone (CLV). Sufficient of the yellow solid was available for one recrystallisation and analysis

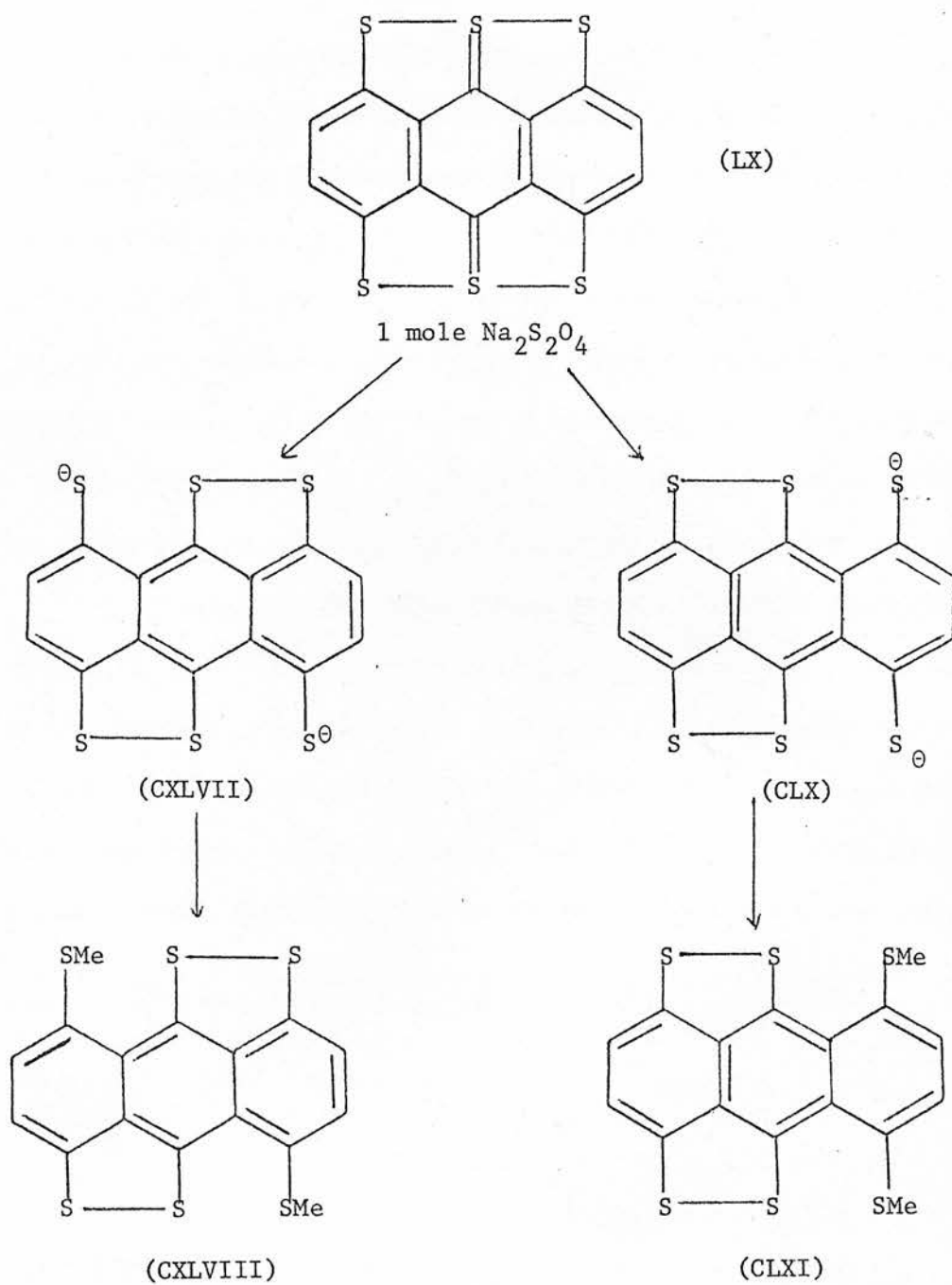


(CLVIII)



(CLIX)

for C and H then gave values close to those required for  $C_{18}H_{18}S_4$ . It was clear that a trace of impurity remained in this product but the identity of the main component seemed no longer in doubt.



SCHEME 20

It was clear from these results that reduction of hexathioanthracene with excess of sodium dithionite had proceeded beyond mere cleavage of the disulphide linkages and that some of the products had been formed by loss of one or two sulphur atoms. It has been assumed in the foregoing discussion that the sulphur atoms removed were those at the 9- and 10-positions of the anthracene system, as is to be expected from the behaviour of 9- and 10-oxygenated anthracene derivatives. Anthracene-9,10-quinones, for example can be reduced to give, ultimately, 9,10-dihydroanthracenes via the sequence:

9,10-quinone → 9,10-dihydroxyanthracene → anthrone → anthracene → 9,10-dihydroanthracene.

Reduction with dithionite is commonly used for the first<sup>(97)</sup> stage of this sequence and has occasionally been used for the second but further reduction normally requires a more powerful reducing agent such as zinc.<sup>(98)</sup> In the corresponding sulphur compounds, however reduction might be expected to proceed more readily at the third stage since a thiocarbonyl group has a lower bond strength than a carbonyl group.

In order to limit the extent of reduction, the quantity of sodium dithionite used in the reaction was reduced from a large excess (as in the foregoing experiments) to an equimolar ratio. It was expected that the dianion (CXLVII) and/or (CLX) would be formed and that methylation would subsequently yield the dimethyl

derivative (CXLVIII) and/or its isomer (CLXI) (Scheme 20).

The reduced solution was heated under reflux with dimethyl sulphate for the same time as in the preceding experiment and a purple solid was isolated. The mass spectrum showed the expected parent ion peak at  $m/e$  394 and subsequent loss of two methyl groups to form  $m/e$  364 (hexathioanthracene). The subsequent breakdown was similar to that of hexathioanthracene itself [loss of 32 (S) and 44 (CS)].

Exact mass measurements on the 394 and 364 peaks confirmed the molecular formulae  $C_{16}H_{10}S_6$  and  $C_{14}H_4S_6$ . The lack of further high mass peaks suggested that the purple solid was largely the expected dimethyl compound(s) and it was unfortunate that insufficient quantity was available after recrystallisation to obtain more spectral or analytical data.

(b) Direct Methylation

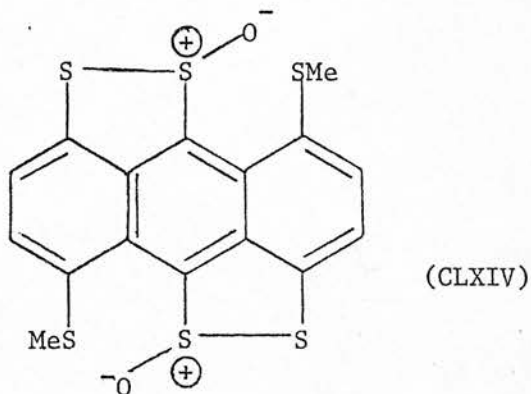
Initially, the direct methylation of hexathioanthracene (LX) was attempted by reaction with dimethyl sulphate but little reaction occurred and starting materials were recovered. Reaction with an excess of the more powerful methylating agent, methyl fluorosulphonate ("magic methyl"), under reflux, gave a green solid which was much more soluble than the starting material but appeared to decompose when recrystallisation was attempted. After being washed with water the product had lost its green colour and thin layer chromatography showed this material to be a mixture showing mainly a purple spot and a blue spot. Column chromatography achieved a separation of the faster moving purple band and the mass spectrum





in various ways of which (CLXIV) is one possibility. Other possibilities would place the O atoms on different S atoms.

$m/e$  426



Since it was not known whether or not the product was a single compound the presence in its mass spectrum of a peak at  $m/e$  410, of intensity greater than that of the 426 ion, introduced ambiguity. This peak is 16 mass units less than the 426 ion and could therefore have two possible origins:

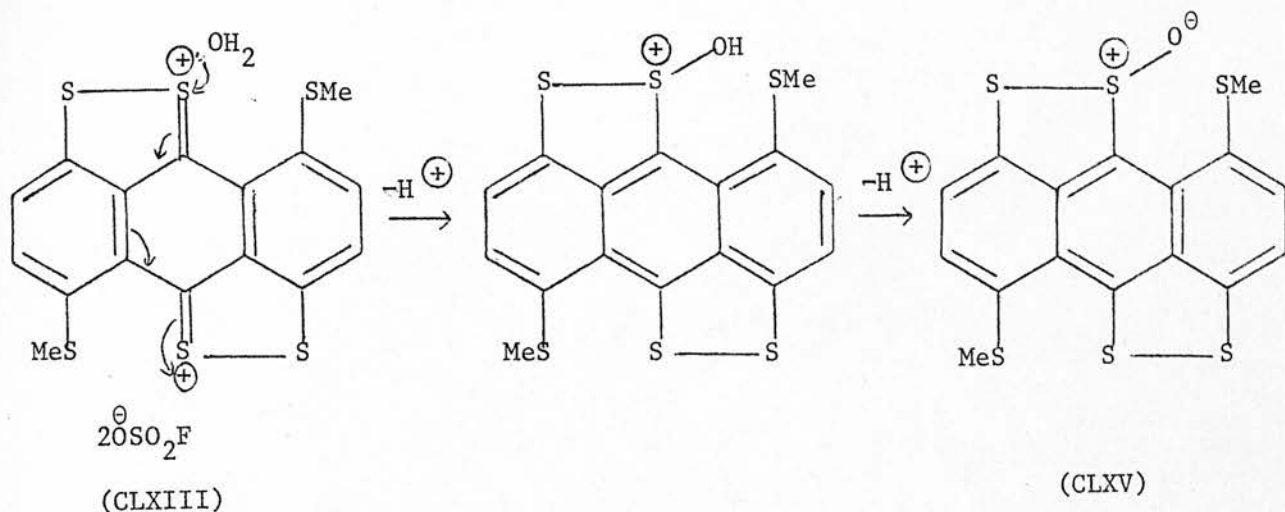
- 1) it could be a fragment peak formed by loss of an oxygen atom from the disulphoxide, or
- 2) it could be the parent ion of an independent monosulphoxide of the dimethyl hexathioanthracene (CLXII).

An attempt was made to separate this product using high speed liquid chromatography and this showed that at least three components were present. Repeated injections of the mixture onto the column and collection of the eluates (U.V. detection) gave three fractions which were evaporated and examined in the mass spectrometer. Fraction 2 was the only one that contained sufficient material to allow a spectrum to be recorded and this showed a parent ion at

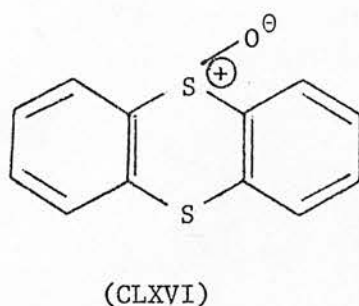
$m/e$  426 with only a very weak fragment peak at  $m/e$  410. The peaks at  $m/e$  394, 379 and 364 were also of lower relative intensity than the corresponding peaks in the mass spectrum of the crude product. This result would seem to indicate that the compound was indeed the sulphoxide (CLXIV) and that the large intensity of the peak at  $m/e$  410 in the mass spectrum of the crude material was due to the admixture with the monosulphoxide. The greater intensity of the  $m/e$  394 peak in the crude sample might be related to the presence of dimethyl hexathioanthracene but could also be caused by fragmentation of the monosulphoxide.

The complexity of the product mixture from this experiment precluded the isolation and characterisation of a pure compound. Any further investigation of the green methylation product might be best carried out by treatment with a reducing agent, such as cold aqueous sodium dithionite which could be expected to give the  $m/e$  394 species as the sole product.

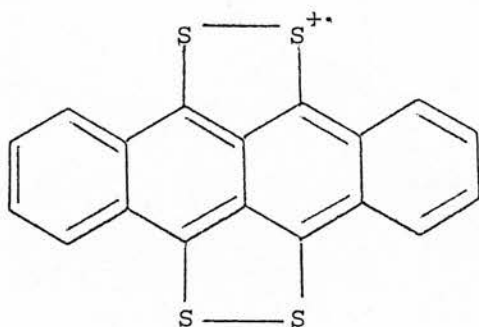
The co-occurrence of dimethyl hexathioanthracene (CCXII) and its mono- and di-sulphoxides in the methylation product of hexathioanthracene, after treatment with water, implies that a redox disproportionation has taken place. Assuming, as seems reasonable, that the initial methylation product is the dication difluorosulphonate (CLXIII), it might be expected that nucleophilic attack by water and loss of two protons would give the monosulphoxide (CLXV) as follows:-



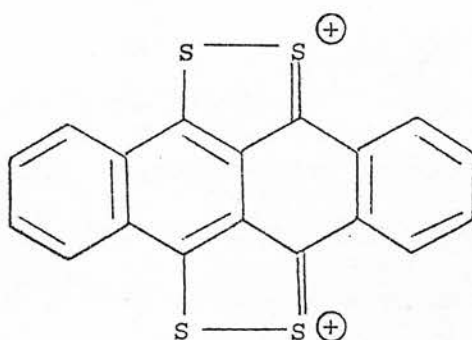
A partial disproportionation to give oxygen-free product and disulphoxide must therefore be assumed to have taken place. A similar disproportionation probably occurs when thianthrene sulfoxide (CLXVI) is dissolved in conc. sulphuric acid<sup>(44b)</sup> (a process which could be expected to generate thianthrene dication) and the solution is diluted with water; the products recovered are thianthrene, thianthrene sulfoxide, and an unidentified, more highly oxygenated, product which is similar to the product obtained from thianthrene disulphoxide by dissolution in sulphuric acid and dilution with water.



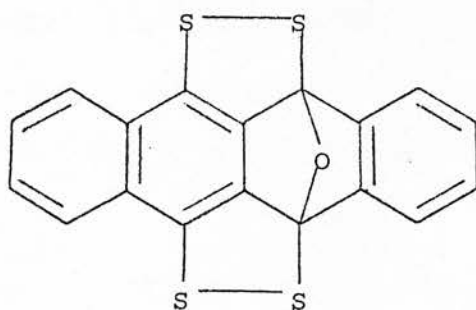
The formation of oxygenated products by treatment of the supposed dication salt (CLXIII) with water recalls the observations of Marschalk<sup>(40)</sup> concerning the reactions of tetrathiotetracene mono- and di-cation salts with aqueous sodium carbonate. Marschalk reported



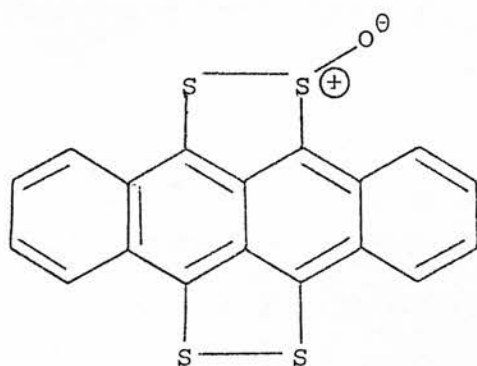
(CLXVII)



(CLXVIII)



(CLXIX)

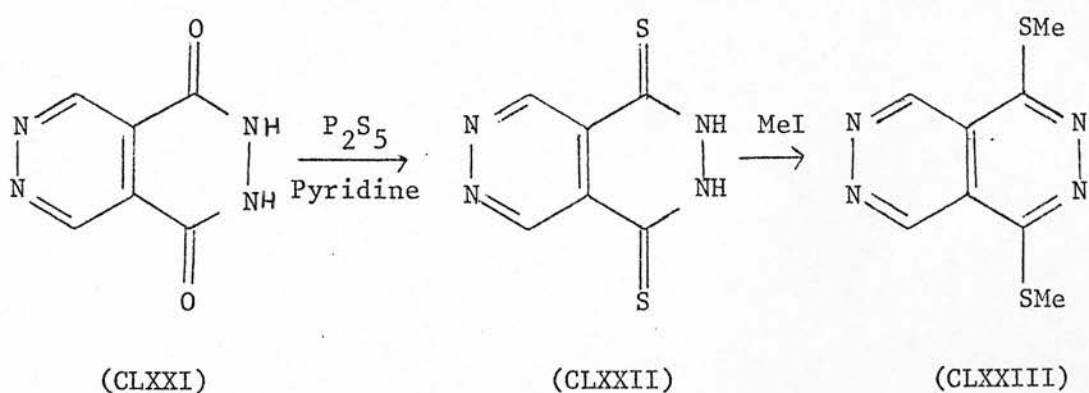


(CLXX)

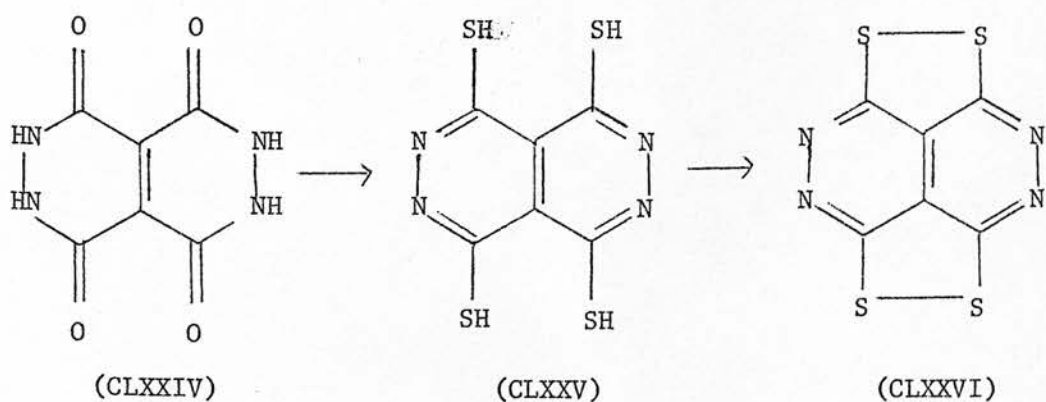
that the monocation salt (CLXVII) gave a green product, analysis of which suggested the formula  $R_2O$  (where  $R$  = tetrathiotetracene) and that the dication salt (CLXVIII) gave a similar green product,  $RO$ . Prinzbach and Futterer<sup>(99)</sup> later suggested that the product ( $RO$ ) might possess the structure (CLXIX) but it now seems more likely that this compound is the sulphoxide (CLXX) possibly accompanied by parent compound and disulphoxide. The product ( $R_2O$ ), obtained from the monocation salt, is probably an equimolecular mixture of tetrathiotetracene ( $R$ ) and ( $RO$ ), a possibility which was appreciated by Marschalk. Such a mixture of parent compound and monosulphoxide is also obtained when thianthrene monocation salts are treated with water.<sup>(100)</sup>

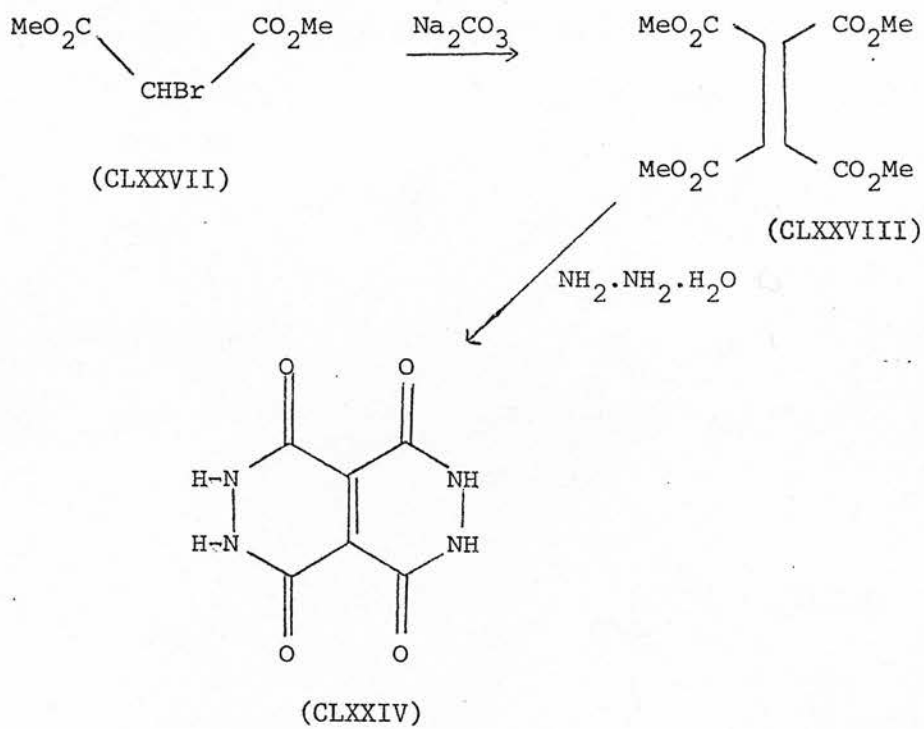
4. The Attempted Synthesis of a Polysulphide Containing a Pyridazino (4,5-d) Pyridazine Nucleus

Pyridazino (4,5-d) pyridazine-1,4-dithione (CLXXII) has been reported by Castle and Di Stefano<sup>(101)</sup> to be formed by phosphorus pentasulphide thiation of pyridazino(4,5-d)pyridazine-1,4-dione (CLXXI). The product was black and was purified by acid-base precipitations and finally by boiling with ethanol.



The existence of this dithione (CLXXII) suggested that the pyridazino(4,5-d)pyridazine-1,4,5,8-(2H, 3H, 6H, 7H) tetrone (CLXXIV) could be a precursor to the novel dithiole system (CLXXVI), the latter being an oxidation product of the tautomeric form (CLXXV) of the tetrathione.



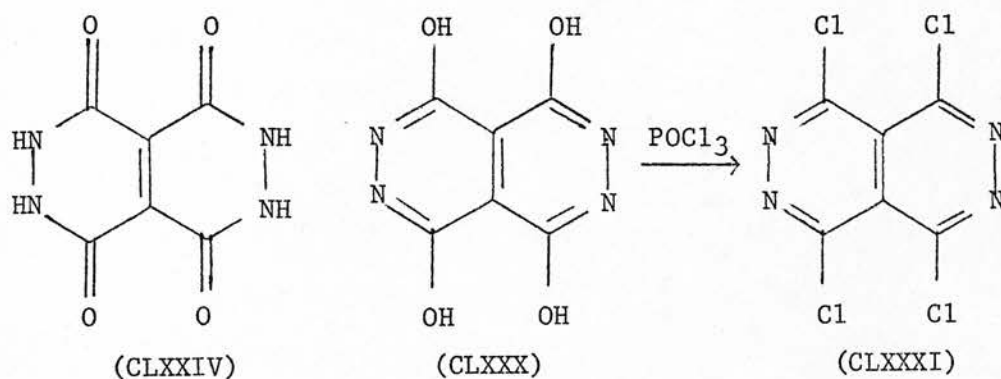


SCHEME 21





An alternative approach to the tetrathione seemed possible invoking conversion of the tetrone into the tetrachloro-compound (CLXXXI) followed by nucleophilic attack by sulphide ion.



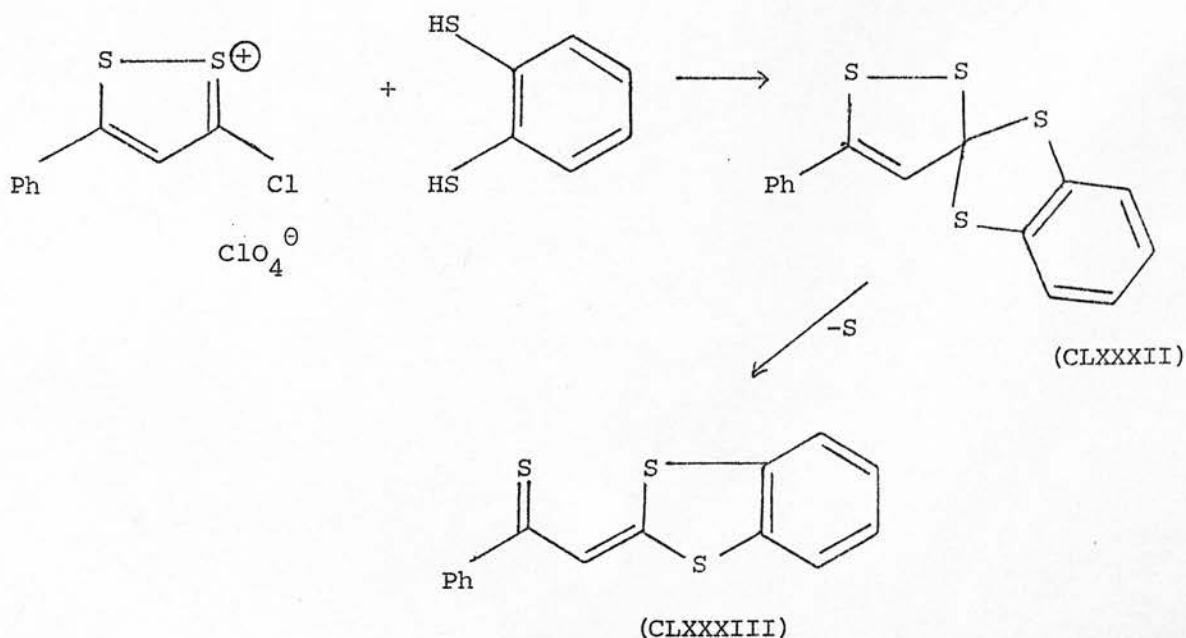
Three methods for the first stage of this route were tried, involving heating of the tetrone with (a) phosphoryl chloride, (b) phosphoryl chloride and phosphorus pentachloride and (c) phenylphosphonic dichloride. None of these methods gave the required tetrachloro-compound (CLXXXI).

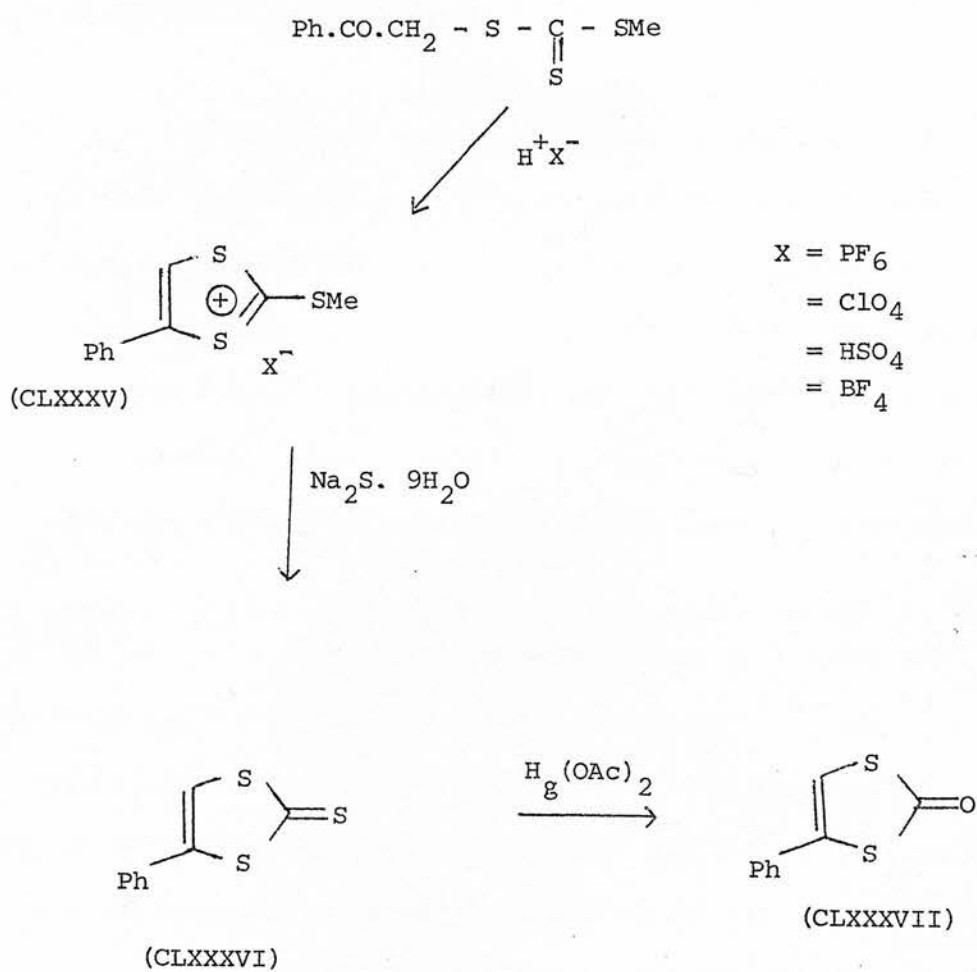
5. Investigations into the Reaction of Acetylenes with 1,2-Dithiole-3-thiones and the Rearrangement of 2-Thioacylmethylene-1,3-dithioles to 1,6,6a-Trithiapentalenes (6a-Thiathiophthens)

A. The Proposed Spiran Intermediate

The mechanism proposed by Davidson (Scheme 1) for the rearrangement of the 2-thioacylmethylene-1,3-dithiole (XVI) to the corresponding 1,6,6a-trithiapentalene (XVII) incorporates the spiro compound (XIX) as the key intermediate. The evidence in support of its involvement was quite strong but, in order to further endorse the mechanism it was considered desirable to generate the same intermediate by an alternative and unambiguous method.

The route that seemed most appropriate was based on the work of Brown<sup>(103)</sup> who showed that 3-chloro-5-phenyl-1,2-dithiolium perchlorate reacts with benzene-1,2-dithiol to give the 2-thio-phenacylidenebenzo-1,3-dithiole (CLXXXIII). This reaction clearly proceeds through the intermediacy of the spiro compound (CLXXXII) which then loses sulphur from the 1,2-dithiole ring.

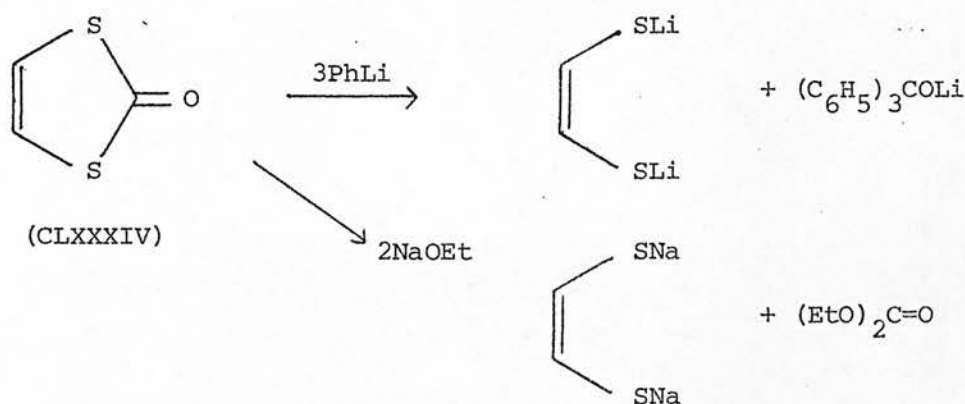




Scheme 22

In order to use this method as a route to the proposed spiran intermediate (XIX) it would be necessary to replace benzene-dithiol by 1-phenylethene-1,2-dithiol or by an alkali-metal salt of the latter.

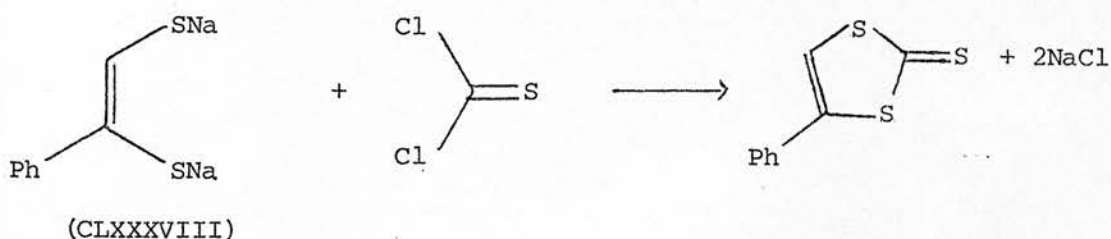
The target compound therefore now becomes the disodium salt of 1-phenylethene-1,2-dithiol and its formation can be conceived along routes similar to those used by Mayer and Gebhardt<sup>(104)</sup> for the synthesis of cis-ethene-1,2-dithiol from 1,3-dithiol-2-one (CLXXXIV).



Extension of this scheme to 4-phenyl-1,3-dithiol-2-one or to 4-phenyl-1,3-dithiole-2-thione might reasonably be expected to provide the disodium or dilithium salt of the required dithiol.

4-Phenyl-1,3-dithiole-2-thione (CLXXXVI) was obtained as shown opposite (Scheme 22) from methyl phenacyl trithiocarbonate by cyclisation<sup>(105)</sup> under acidic conditions using either hexafluorophosphoric acid, fluoroboric acid, sulphuric acid, or perchloric acid and treatment of the resulting 2-methylthio-1,3-dithiolium salt (CLXXXV) with sodium sulphide.

Following the conditions used by Mayer and Gebhardt for the reaction of 1,3-dithiol-2-one, 4-phenyl-1,3-dithiole-2-thione was treated with sodium ethoxide and an ether-insoluble solid was obtained. To check whether the desired product had been formed a sample of the solid was allowed to react with thiophosgene which was expected to reconvert the sodium dithiolate (CLXXXVII) into the original dithiolethione.



T.l.c. analysis of this reaction mixture showed only a trace of the thione thus showing that only a small quantity of the desired dithiolate (CLXXXVIII) had been produced.

Since little reaction was obtained using the thione (CLXXXVI) it was decided to adhere more closely to the procedure of Mayer and Gebhardt and to use 4-phenyl-1,3-dithiol-2-one as starting material for preparation of the dithiol. The required dithiolone (CLXXXVII) was readily obtained from the thione (CLXXXVI) by reaction with mercuric acetate. Treatment of the dithiolone with sodium ethoxide again gave an ether-insoluble solid from which only traces of the dithiolethione were produced after reaction with thiophosgene. Phenyl-lithium was then substituted for sodium ethoxide and once more an ether-insoluble product was obtained. Investigation of the organic extracts indicated the presence of triphenyl carbinol and starting material. The triphenyl carbinol

would have been an expected by product from the reaction had it been successful but reaction of the ether-insoluble solid with thiophosgene failed to produce 4-phenyl-1,3-dithiole-2-thione. Further attempts to obtain 1-phenylethene-1,2-dithiol were abandoned.

B. The Effect of Vulcanisation Accelerators on the sulphur-catalysed Rearrangement

Davidson's observation<sup>(29)</sup> that vulcanisation accelerators increase the rate of the sulphur catalysed rearrangement of 2-thioacetylmethylene-1,3-dithioles has been mentioned in the introduction (P.8). Zinc N,N-dialkyldithiocarbamates are widely used as vulcanisation accelerators and were found to be among the most effective co-catalysts for the rearrangement. It is known<sup>(106)</sup> that the dithiocarbamates of other metals vary in their activity as vulcanisation accelerators; those of Zn(II), Cd(II), Cu(II) and Fe(III) are reported to be active at 140° while those of Ni(II), Co(III) and Cr(III) are inactive at this temperature. It seemed worthwhile, therefore, to compare the activity of some of these complexes as catalysts for the rearrangement since this might further establish the mechanistic similarity of the vulcanisation to the rearrangement processes.

The results of this study are shown in Table One from which it can be seen that all the dithiocarbamates investigated had some accelerating effect on the rearrangement. The zinc and iron complexes were the most effective, the cobalt and nickel complexes were the least effective, and the copper and cadmium complexes were of intermediate activity. There is thus a broad similarity to the activity of these complexes in vulcanisation though it would

seem that the rearrangement provides a more discriminating test of activity, being capable of differentiating the effects of zinc and iron from those of cadmium and copper.

In measuring the catalytic effect of sulphur alone, it was noticed that different batches of the solvent, xylene, gave different results; the rearrangement occurred much more rapidly in batches of xylene that contained low boiling impurities while in "Analar" xylene which contained only high boiling impurities the rate of rearrangement was much lower and about the same as in carefully purified chlorobenzene. Accordingly, "Analar" xylene was used in subsequent experiments. It seemed possible that the low boiling impurities were promoting sulphur ring-opening in a manner analogous to that proposed for vulcanisation accelerators. An attempt was therefore made to separate the impurities by means of a spinning band distillation column but no success was achieved and the substances responsible for the catalytic effect remain unidentified.

C. The Possible Intermediacy of Thioacylcarbenes in the Reaction of Acetylenes with 1,2-dithiole-3-thiones

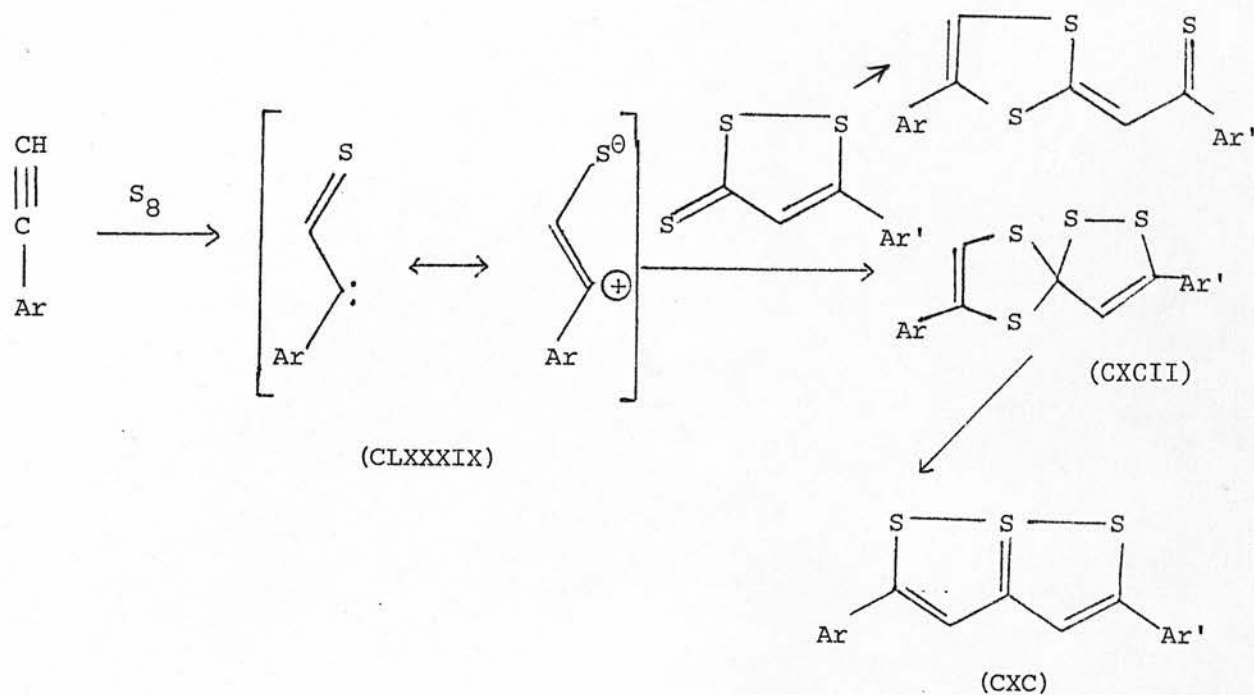
Davidson claimed that the formation of 2-phenyl-5-p-methoxy-phenyl-1,6,6a-trithiapentalene (XXIII) by sulphur-catalysed rearrangement of 4-p-methoxyphenylthiophenacylidene-1,3-dithiole (XXIV) occurred more slowly in boiling xylene than did the formation of a comparable amount of 1,6,6a-trithiapentalene by direct reaction of p-methoxyphenylacetylene with 5-phenyl-1,2-dithiole-3-thione in the presence of sulphur. He concluded that there was an additional route to the 1,6,6a-trithiapentalene other than via the isomeric 1,3-dithiole and suggested that this might involve the

formation of a thioacylcarbene which would be trapped by the dithiolethione, thus leading directly to the spiran intermediate (XIX) (See introduction pp 9-12).

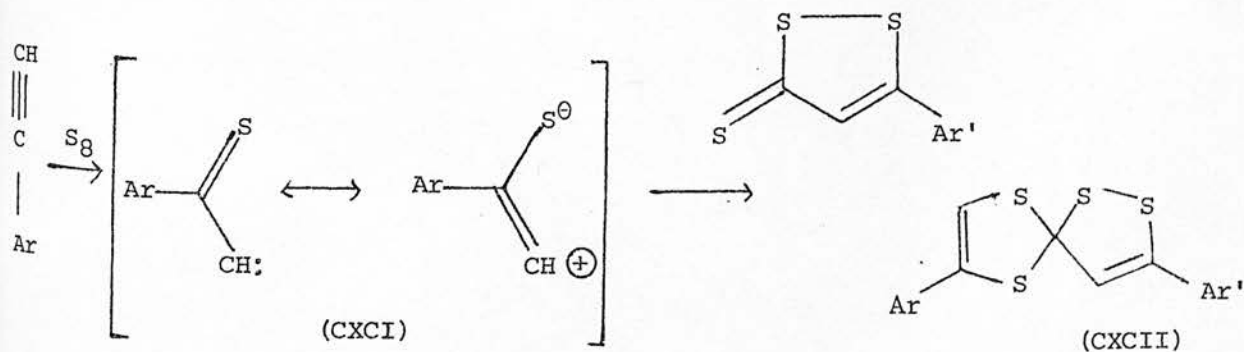
Re-examination of Davidson's results showed that his original claim concerning the relative rates of the rearrangement and of the direct reaction did not appear to be clearly substantiated. In particular, the conditions under which the direct reaction was carried out were such that a reasonable material balance was not obtained. Accordingly the reaction of p-methoxyphenylacetylene with 5-phenyl-1,2-dithiole-3-thione was reinvestigated using "Analar" xylene as the solvent and with lower concentrations of reactants than those used by Davidson. (This has the effect of minimising the formation of uncharacterisable by-product). In the absence of sulphur, a 31% yield of the 1,3-dithiole (XXIV) was obtained after 3h, no "trithiapentalene" was formed and 62% of the dithiolethione was recovered. In the presence of sulphur, but under otherwise comparable conditions, the yield of 1,3-adduct increased to 42%, "trithiapentalene" was formed in 28% yield and only 26% of the thione was recovered. Thus the total yield of adducts increased from 31% to 70% when sulphur was present.

This result neither substantiates nor refutes Davidson's claim but it shows quite conclusively that sulphur can participate in the initial formation of adducts from arylacetylenes and 1,2-dithiolethiones; it is not merely a catalyst for the rearrangement of one type of adduct to the other. The thioacylcarbene mechanism proposed by Davidson provides an acceptable rationalisation:-

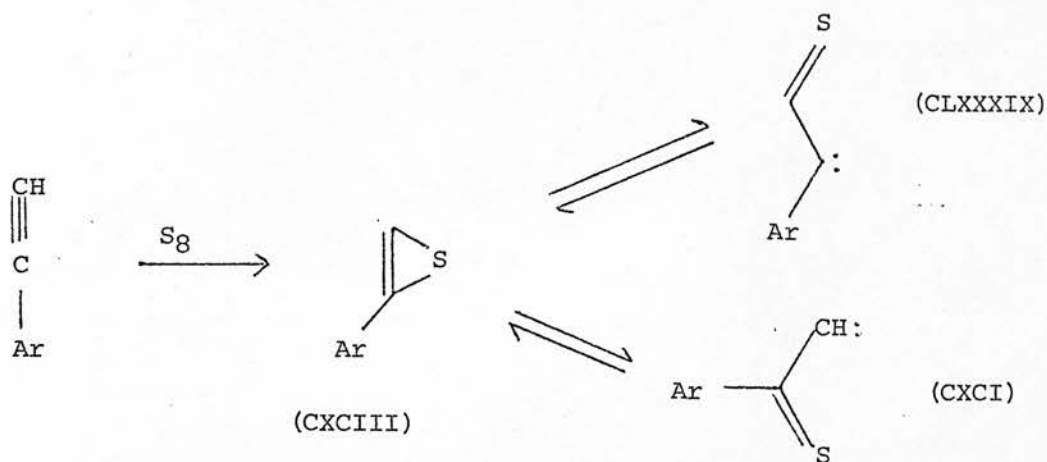




In all previous discussions of the thioacylcarbene mechanism, this reactive intermediate has been formulated as a thioformylarylene carbene (CLXXXIX) but it could equally well be formulated as a thioaroyl carbene (CXCI) and this might be expected to form the same spiran intermediate (CXCII) by addition to the dithiolethione.



Indeed it is possible that the product of interaction of sulphur and the arylacetylene might be the thiirene (CXCI) which could combine with the dithiolethione in the same way as either carbenes (CLXXXIX) or (CXCI) and is predicted to be the more stable valence tautomer<sup>(107)</sup>. Alternatively, the thiirene might be involved in the reaction as an intermediate which provides a route for interconversion of (CLXXXIX) and (CXCI).

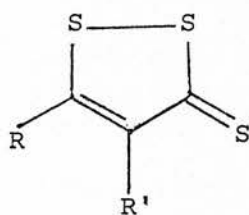


Rees and his coworkers<sup>(108)</sup> have shown that such interconversions take place in the thioacylcarbenes generated by  $\text{Fe}_2(\text{CO})_9$ -promoted thermolysis of 4,5-diaryl-1,2,3-thiadiazoles.

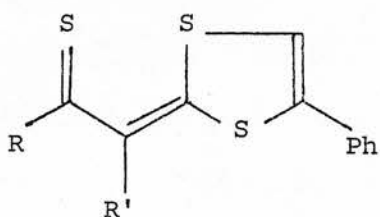
Davidson showed that when the carbene (CLXXXIX; Ar = Ph) was generated by thermolysis of 4-phenyl-1,2,3-thiadiazole in the presence of an equimolar quantity of 5-phenyl-1,2-dithiole-3-thione, the expected "trithiapentalene" (CXC) was formed in 20% yield. It was therefore of interest to generate the isomeric carbene (CXCI; Ar = Ph) by thermolysis of 5-phenyl-1,2,3-thiadiazole and to investigate its behaviour in the presence of the dithiolethione. The required thiadiazole was obtained by treatment of phenylacetaldehyde semicarbazone with thionyl chloride and, in

lower yield, by similar treatment of the ethoxycarbonylhydrazone.<sup>(109)</sup> Thermolysis at 200° in the presence of an equimolar quantity of 5-phenyl-1,2-dithiole-3-thione led to complete disappearance of the thiadiazole in 1.5h but t.l.c. then showed that only traces of the "trithiapentalene" had been formed. After addition of more thiadiazole (3 equivalents) and further heating a 5% yield (based on thiadiazole) of "trithiapentalene" was obtained and 40% of the thione was recovered. The yield of "trithiapentalene" based on thiadiazole was smaller in this experiment, using the 5-phenyl-compound, than in Davidson's experiment using the 4-phenyl-compound. Thus the thioacylcarbene (CXCI) appears to react less efficiently with the dithiolethione than does its isomer (CLXXXIX).

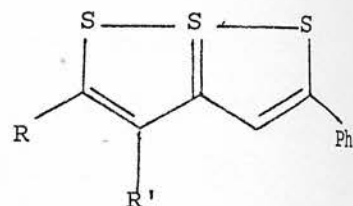
These experiments with thiadiazoles were designed as a test of the possibility that "trithiapentalenes" could be formed by reaction of thioacylcarbenes with 1,2-dithiole-3-thiones. Their validity however depends on the assumption that the thiadiazoles do not decompose to give nitrogen, sulphur, and phenylacetylene. This mode of decomposition has been observed in the corresponding 1,2,3-selenadiazoles and is recommended as a preparative route to arylacetylenes.<sup>(110)</sup> Accordingly, control experiments were carried out in which 4- and 5-phenyl-1,2,3-thiadiazoles were heated alone at 200°. The thermolysis products including the fractions that condensed on the cooler parts of the vessel, were examined by gas chromatography but no trace of phenylacetylene was detected.



(CXCIV)



(CXCV)



(CXCVI)

a : R, R', = (CH<sub>2</sub>)<sub>3</sub>

b : R, R' = (CH<sub>2</sub>)<sub>4</sub>

c : R = t - Bu; R' = CH<sub>3</sub>

d : R = t - Bu; R' = neo - C<sub>5</sub>H<sub>11</sub>

e : R = R' = CH<sub>3</sub>

Scheme 23

D. The Effect of Alkyl Substituents in the 1,2-dithiole-3-thione

The generalisations which were made in the introduction concerning the reactions of 1,2-dithiole-3-thiones with arylacetylenes are strictly applicable only to the 5-aryldithiolethiones. Davidson showed that the behaviour of dithiolethiones (CXCIV), containing aliphatic substituents in the 4- and 5-positions was different in several respects and his main findings are summarised below.

- i) The 4,5-cyclopenteno-compound (CXCIVa) gave a 2-thioacyl-methylene-1,3-dithiole (CXCVa) that did not rearrange to a "trithiapentalene" under any circumstances including heating at 200° and treatment with sulphur in boiling xylene.
- ii) The 4,5-cyclohexeno-compound (CXCIVb) reacted with phenylacetylene in boiling xylene to give only the "trithiapentalene" (CXCVIb), even in the absence of added sulphur. The isomeric 1,3-dithiole (CXCIVb) was obtained by reaction of the thione with phenylpropionic acid in boiling benzene and was shown to rearrange to (CXCVIb) even in the absence of added sulphur on more prolonged boiling in benzene.
- iii) The 5-t-butyl-4-alkyl -compounds (CXCIVc) and (CXCIVd) yielded only "trithiapentalenes" (CXCVIc) and (CXCVID) even by reaction with phenylpropionic acid in boiling dichloromethane.

Thus there appeared to be no consistent pattern of behaviour in aliphatic dithiolethiones though, with the notable exception of the cyclopenteno-compound (CXCIVa) all the compounds investigated yielded "trithiapentalenes" more readily than their 5-aryl counterparts.

Since all of the compounds investigated by Davidson contained structural features which could be regarded as atypical [fused rings

in (CXCIVa) and (CXCIVb) bulky alkyl groups in (CXCIVc) and (CXCIVd)] it seemed desirable to study an unexceptional aliphatic dithiolethione in order to discover which of the above patterns of behaviour should be regarded as normal. It was also desirable to purify the thione and the solvent carefully in order to exclude sulphur and/or other substances which might catalyse the rearrangement (CXCv) to (CXCvI). (In Davidson's work the solvent, xylene was not specially purified and the thiones (CXCIVc) and (CXCIVd) being liquids might well have contained traces of sulphur or other impurities which would have been very difficult to remove).

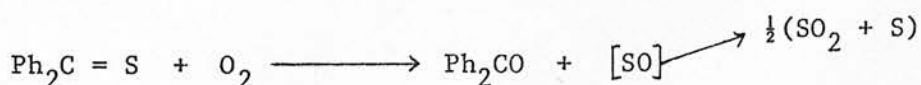
Accordingly the 4,5-dimethyl-compound (CXCIVe) was chosen for further study since it contains small alkyl groups and crystallises well. It was obtained by reaction of ethyl 2-methyl-3-oxobutanoate with phosphorus pentasulphide and was purified after regeneration from its mercuric chloride complex by chromatography and repeated recrystallisation to constant melting point. Chlorobenzene was chosen as the solvent since it can be more easily purified than xylene by treatment with concentrated sulphuric acid (see experimental).

The reaction of the thione with phenylacetylene was first attempted in "Analar" benzene but no change was observed after 5h at the boiling point. In boiling chlorobenzene, a red product was detectable by t.l.c. after 1.5h and working up after 30h, when reaction was almost complete, gave the "trithiapentalene" (CXCvIe) as the main product; none of the isomeric product (CXCvIe) was obtained. A minor oily product showed  $m/e$  236 which corresponds to a diphenylthiophene ( $2 \times \text{PhC} \equiv \text{CH} + \text{S}$ ) though the mass spectroscopic

fragmentation pattern did not correspond to those of either 2,4- or 2,5-diphenylthiophene both of which are solids.

The identification of the main product as (CXCVIe) follows from the chemical shift of the dithiole ring proton ( $\tau$  2.00) which is typical of H-3 (or 4) of a "trithiapentalene" rather than H-5 ( $\tau$  2.7 - 3.0) of the 1,3-dithioles (CXCv). Moreover, the phenyl protons showed splitting into low-field (ortho) and high-field (meta and para) multiplets which is characteristic of 2-phenyl groups in "trithiapentalenes" but not of 4-phenyl groups in the 1,3-dithioles (CXCv).

It seemed possible that the formation of "trithiapentalene" in this experiment with carefully purified starting materials might be due to liberation of elemental sulphur by decomposition of a small amount of the dithiolethione. Since dithiolethiones bearing alkyl substituents are likely to be less stable than their aryl counterparts, such an effect is likely to be more noticeable with the alkyl compounds. The isolation of the minor product showing  $m/e$  236 lent support to such a suggestion since it showed that an atom of sulphur had been removed from the thione. Liberation of sulphur from thiones is a process which has been frequently reported,<sup>(112)</sup> though not previously for 1,2-dithiole-3-thiones; oxygen is commonly involved in the process, as shown below for thiobenzophenone, and light is often necessary as in the photo-oxidation of 4H-pyran- and -thiopyran-4-thiones<sup>(113)</sup>





In order to check the possibility that such a thermal or photo-oxidative process might be involved in the reaction of the thione (CXCIVe) with phenylacetylene, the experiment in purified chlorobenzene was repeated with exclusion of oxygen and light. Despite these precautions, however, the same products were obtained and no trace of the 1,3-dithiole (CXCVe) was detected.

As a means of obtaining the elusive 1,3-dithiole (CXCVe), from the thione (CXCIVe), phenylacetylene was replaced by phenylpropionic acid. In the first experiment, the reactants were heated together in dichloromethane but the initial product showed a dark baseline spot on t.l.c., indicating that decarboxylation was not occurring. However, after 20h an additional spot of much lower polarity appeared and at this point the solvent was changed to benzene and heating under reflux was continued in order to decarboxylate the product. Chromatography of the reaction mixture gave a trace of the "trithiapentalene" but the major chromatographic band yielded a brown solid. The infra-red spectrum of this solid showed that decarboxylation had occurred but the p.m.r. spectrum showed it to be a mixture of the required adduct and unreacted dithiolethione. Complete separation of these two compounds could not be achieved.

In an attempt to drive the reaction to completion the reaction was repeated in boiling benzene from the outset. This afforded a better overall yield but the product contained approximately equal amounts of "trithiapentalene" and the adduct (CXCVe) which was still contaminated with the original thione.



Although no pure sample of the adduct (CXCVe) could be isolated, it is nevertheless clear from these experiments that the behaviour of 4,5-dimethyl-1,2-dithiole-3-thione is analogous to that of the 4,5-cyclohexeno-compound; both of these thiones react with phenylacetylene at ca  $140^{\circ}$  (boiling xylene or chlorobenzene) to give a "trithiapentalene", the corresponding 2-thioacetylmethylene-1,3-dithiole being a relatively labile compound which rearranges slowly even at  $80^{\circ}$  (boiling benzene). It seems likely that this is the normal pattern of behaviour for alkyl substituted dithiole-thiones but there is as yet no evidence as to whether the "trithiapentalene" is formed directly at  $140^{\circ}$  (i.e. by 1,2-cycloaddition to the thione group and opening of the four-membered ring - introduction P6) or via the isomeric 1,3-dithiole, or via the intermediacy of a thioacylcarbene. Likewise, there is no evidence concerning the mechanism of rearrangement of the 2-thioacetylmethylene-1,3-dithioles bearing alkyl groups on the thioacetylmethylene moiety. It may be that, like their aryl analogues, these adducts rearrange by a catalytic mechanism involving sulphur or some other, as yet unidentified, agent or that the rearrangement is entirely intramolecular and independent of catalytic agents.

EXPERIMENTAL

NOTES

- 1) The following instruments were used for obtaining spectroscopic data.

Infrared: Unicam SP 200 Infrared spectrophotometer.

Perkin-Elmer 157G Grating Infrared Spectrophotometer.

Proton Magnetic Resonance: Varian HA 100 n.m.r. spectrometer.

Mass: A.E.I. MS902 Mass Spectrometer.

- 2) The alumina used for column chromatography was "Activated Alumina Type H" from Laporte Industries Ltd.
- 3) The melting points are uncorrected.

## SECTION 1

### PREPARATION OF COMPOUNDS CONTAINING A BENZENE NUCLEUS

#### The Preparation of Benzo-1,2-dithiole-3-thione

o-Chlorobenzyl chloride (1.61g, 0.1 mol) and elemental sulphur (1.60g, 0.06 mol) were dissolved in N,N-dimethylformamide and heated under reflux, until t.l.c. showed that the starting material had all reacted, and an orange spot had appeared on the plate. The dark solution was poured into water, extracted into ether, and dried over anhydrous magnesium sulphate. Evaporation of the solvent gave a red oil, which, on addition of ethanol and scratching, yielded orange-red crystals. Chromatography on activated alumina, using benzene as eluant and recrystallisation from benzene gave the product as orange needles, m.p. 97-98°C (lit, 94-96°C).<sup>(114)</sup> The infra-red spectrum was identical with that of an authentic specimen.

| <u>Volume of Solvent</u> | <u>Yield</u> | <u>Time of Reflux</u> |
|--------------------------|--------------|-----------------------|
| 25 ml.                   | 15%          | 24 h                  |
| 15 ml.                   | 30%          | 48 h                  |

#### The Preparation of 1,3,5-Tribromomesitylene

Prepared by the method of G.F. Hennion and J.G. Anderson by<sup>(71)</sup> the action of bromine on mesitylene, using iron as catalyst, yield 25%, m.p. 222-224°C. ((toluene) lit m.p. 222-224°C)  
p.m.r.: (CDCl<sub>3</sub>),  $\tau$  : 7.36 (s, Ar.CH<sub>3</sub>).

#### The Preparation of 1,3,5-Tribromo-2,4,6-tris(bromomethyl)benzene

1,3,5-Tribromomesitylene (5.0g, 0.01 mol) was dissolved in carbon tetrachloride (500 ml), and bromine (2.5 ml, 7.95g, 0.1 mol) added dropwise to the solution. The reaction vessel was irradiated

with a strong light for 24h, and after evaporation of the solvent, a light brown solid (7.4g) was obtained, which was recrystallised from ethanol to give the product (3.9g) as off-white needles. The product was not analysed because of the possibility of higher brominated compounds being present.

p.m.r. : ( $\text{CDCl}_3$ ),  $\tau$  : 5.10 (S, Ar. $\text{CH}_2$ .Br)

mass spectrum:  $m/e$  (% abundance) : 600-588 (P, septet, 10% for 594; 519-509 (sextet, 100% for 513 and 515); 435 (multiplet, 25%); 355 (multiplet, 10%); 275 (multiplet, 10%); 217 (multiplet, 15%); 196 (multiplet, 20%). ( $\text{C}_9\text{H}_6^{79}\text{Br}_6$  requires P = 588).

$m^*$  : 300 (515  $\rightarrow$  435); 290 (435  $\rightarrow$  355).

The Preparation of Benzo(1,2-C; 3,4-C'; 5,6-C'')tris(1,2)dithiole-1,4,7-trithione

1,3,5-Tribromo-2,4,6-tris(bromomethyl)benzene (1.38g, 0.002 mol), dimethylformamide (50 ml), and sulphur (1.12g, 0.004 mol), were heated under reflux for seven days. The light brown solution was filtered to give a reddish-brown solid (0.94g), which was insoluble in many organic solvents (1,2,4-trichlorobenzene, *o*-dichlorobenzene, nitrobenzene, dimethyl sulphoxide, ethyl benzoate, methoxyethanol, acetonitrile, acetic acid and quinoline).

mass spectrum:  $m/e$  (% abundance) : 396 (P, 80%); 393 (30%); 390 (50%); 387 (60%); 320 (100%).

A fraction of the product was sublimed under vacuum (0.1 mm Hg, 340°C) to give a red solid.

mass spectrum:  $m/e$  (% abundance): 396 (12%); 393 (15%); 390 (60%); 387 (100%); 354 (50%); 347-343 (multiplet, 343 max, 60%); 333 (60%); 320 (40%); 318-314 (multiplet, 40%); 308 (45%); 297 (50%).

( $\text{C}_9\text{S}_9$  requires P = 396).

The series of peaks at increments of 3 mass units below  $m/e$  396 is due to solvent participation in the reaction. ( $N.CH_3$  introduced into compound rather than S).

#### The Preparation of 2,5-Dimethyl-p-benzoquinone

Prepared by the method of L.I. Smith, et al.<sup>(115)</sup> from 2,5-Dimethylaniline m.p. = 123-124°C (ethanol) (lit, 123-125°C) as yellow needles.

#### The Reaction of 2,5-Dimethyl-p-benzoquinone with Sulphur

##### a) With ethyl benzoate as solvent

2,5-Dimethyl-p-benzoquinone (2.5g, 0.018 mol), sulphur (5.9g, 0.023 mol), and ethyl benzoate (25 ml) were heated under reflux for 17 h. T.l.c. (silica-benzene) showed the gradual disappearance of starting materials and the growth of three large spots (r.f. 0.6, 0.2 and 0.05) after development in iodine vapour. The reaction mixture was cooled, and a black solid (3.7g) filtered off.

Chromatography of the concentrated filtrate on activated alumina with petrol-benzene mixtures as eluants gave rise to:-

- 1) a faint yellow band, (23 ml) of high boiling liquid. An infra-red spectrum proved the product to be ethyl benzoate (90% light petroleum b.p. 40-60°C, 10% benzene);
- 2) A yellow band which on evaporation of solvent gave yellow crystals (10 mg, m.p. 110-113°C). The m.p. and absence of infra-red absorption suggested that this was sulphur.  
(benzene 20% - light petroleum b.p. 40-60°C 80%);
- 3) A brown band which yielded an oily solid (0.05g) (chloroform);
- 4) A red band which, on evaporation of solvent, gave a black solid (0.12g, m.p. >300°C) (methanol).

Extraction of the solid filtered from the reaction mixture with benzene, gave an insoluble solid (3.2g) and on evaporation of the solvent, yellow crystals (0.5g) which had no bands in the infra-red spectrum (sulphur).

A mass spectrum was obtained on the insoluble solid.

$m/e$  (% abundance): 324 (P+2, 25%); 322 (P, 100%); 291 (10%); 289 (35%); 230 (25%); 161 (10%); 160 (10%); 150 (20%).

$m^*$ : 259 (322  $\rightarrow$  289). The spectrum also showed contamination with elemental sulphur.

Exact mass measurement:

$M^+$  = 321.83789 ( $C_8H_2^{32}S_6O_2$  requires 321.83791.)

$M^+$  = 323.83389 ( $C_8H_2^{32}S_5^{34}SO_2$  requires 323.83370).

Soxhlet extraction in acetone followed by recrystallisation from ethyl benzoate afforded sufficient green crystalline material for one analysis only.

#### Analysis

Found : C, 32.0; H, 0.8%

$C_8H_2O_2S_6$  requires : C, 29.8; H, 0.6%.

#### b) With N,N-Dimethylformamide as Solvent

The quinone (2.5g, 0.018 mol), sulphur (5.9g, 0.023 mol), and dimethylformamide (25 ml) were heated under reflux for 17 h. The mixture was cooled, and filtered, to yield a black solid (1.6g). The filtrate was concentrated and chromatographed on deactivated (5%) alumina, to give six fractions none of which yielded more than 0.08g of material and which were not investigated further.

The insoluble dark solid was heated to 300°C in the mass spectrometer but no spectrum was obtained. The residue remaining on

the probe was difficult to burn completely.

c) With Dimethyl sulphoxide as Solvent

2,5-Dimethyl-p-benzoquinone (2.5g, 0.018 mol), dimethyl sulphoxide (50 ml), and sulphur (5.9g, 0.023 mol), were heated under reflux for 17 h. The reaction mixture was cooled, filtered to remove the black solid (7.4g), poured into water, and extracted with hot chloroform. The extract was dried over anhydrous magnesium sulphate, and evaporated under reduced pressure to yield a yellow solid (0.5g) which had no bands in the infra-red spectrum and, by mass spectroscopy, proved to be elemental sulphur.

A mass spectrum was run on the black solid and showed only the presence of elemental sulphur even on heating to 300°C.

The Reaction of  $\alpha,\alpha',2,3,5,6$ -Hexachloro-p-xylene with Sulphur

a) With N,N-dimethylformamide as Solvent

$\alpha,\alpha',2,3,5,6$ -Hexachloro-p-xylene (1.56g, 0.005 mol), and sulphur (1.92g, 0.06 mol), were heated under reflux, for 4 h, in N,N-dimethylformamide (50 ml). The reaction mixture was poured into water, and extracted into chloroform, and the extract was dried over anhydrous magnesium sulphate. The chloroform was removed under reduced pressure and the product chromatographed on activated alumina to give:-

- 1) a purple band which yielded a purple solid (0.55g) (light petroleum b.p. 40-60°C)

$m/e$  (% abundance): 401 (P+2, 60%); 399 (P, 100%); 367 (30%); 337 (45%); 335 (75%); 322 (55%); 320 (95%); 307 (30%); 305 (60%); 295 (20%); 294 (25%); 293 (50%); 292 (30%); 247 (60%).



$m^*$ : 322 (399  $\rightarrow$  364); 305 (335  $\rightarrow$  320); 268 (322  $\rightarrow$  294)

exact mass measurement;  $M^+$ , 398.8222 ( $C_{10}H_6^{35}Cl N S_7$  requires 398.8234).

2) A purple-red band which gave a dark brown solid (0.30g).

$m/e$  (% abundance): 364 (10%); 362 (50%); 360 (100%); 358 (75%); 319 (40%); 318 (35%); 317 (70%); 316 (55%); 315 (55%); 314 (40%); 283-279 (multiplet, max peaks 280 and 282 (45%)).

$m^*$  279 (358  $\rightarrow$  314).

The molecular formula was substituted into a computer programme which simulated the theoretical isotope pattern. This proved to be identical with that found on the mass spectrum.

exact mass measurement:  $M^+$ , 357.9623 ( $C_{12}H_{14}^{35}Cl_4 N_2 S$  requires  $M^+$ , 357.9632);

$M^+$ , 359.9594 ( $C_{12}H_{14}^{35}Cl_3^{37}Cl N_2 S$  requires  $M^+$ , 359.9602);

$M^+$ , 361.9586 ( $C_{12}H_{14}^{37}Cl_2^{35}Cl N_2 S$ , requires  $M^+$ , 361.9573).

3) An orange band yielding a dark solid (0.11g).

$m/e$  (% abundance): 392 (P+2, 60%); 390 (P, 100%); 388 (P-2, 65%); 357 (35%); 355 (90%); 353 (55%); 348 (12%); 346 (20%); 344 (22%); 319 (45%); 317 (55%); 315 (40%); 221 (25%).

$m^*$  323 (390  $\rightarrow$  355); 321 (388  $\rightarrow$  353); 287 (355  $\rightarrow$  319);

285 (353  $\rightarrow$  317);

4) A brown band which gave a brown solid (0.07g).

$m/e$  (% abundance): 413 (P+2, 40%); 411 (P, 90%); 256 (100%); 224; 196 - sulphur pattern.

exact mass measurement:  $M^+$ , 410.8499 ( $C_{11}H_9N^{32}S_8$  requires  $M^+$ , 410.8501)

$M^+$ , 412.8461 ( $C_{11}H_9N^{32}S^{34}S$  requires  $M^+$ , 412.8459).

5) An orange red band which gave a reddish solid (0.22g).

$m/e$  (% abundance); 321 (100%); 319 (100%); 256 (80%).

b) With Sulpholane as Solvent

$\alpha, \alpha', 2, 3, 5, 6$ -Hexachloro-p-xylene (1.56g, 0.005 mol), sulphur (1.92g, 0.06 mol), and sulpholane (25 ml), were heated under reflux for 8 h. The reaction mixture was poured into water and extracted with chloroform. A black solid (2.5g) which was insoluble in both phases, was filtered off. Mass spectroscopy and infra-red spectroscopy showed this to be largely a mixture of starting materials. The chloroform extract was dried and evaporated under reduced pressure to give an oily solid (0.6g) which proved to be a mixture of sulpholane, sulphur, and hexachloro-p-xylene (from i.r. and mass spectra).

## SECTION 2

### PREPARATION OF COMPOUNDS CONTAINING A NAPHTHALENE NUCLEUS

#### The Attempted Preparation of Naphtho(1,8-cd:4,5-c'd')bis(1,2-dithiole)

a) 1,5-Bis(chlorodithio)naphthalene was prepared by an adaption of the method of F. Fehér, R. Glinka and F. Malcharek.<sup>(77)</sup>

Naphthalene-1,5-dithiol (0.96g, 0.005 mol) which had been recrystallised from ether (m.p. 119 - 120°; lit 118 - 121°<sup>(116)</sup>) was dissolved in anhydrous carbon tetrachloride (50 ml) and dropped with stirring into freshly distilled dichloromonosulphane (70 ml) at room temperature. The addition was complete after 15 minutes and the homogeneous solution was allowed to stand overnight. The volatile components were removed in vacuo to yield a red oil (1.49g).

b) The crude oil (1.49g, 0.005 mol), was dissolved in anhydrous methylene dichloride and dropped into a two-necked flask containing aluminium chloride (0.61g, 0.005 mol) which was covered by anhydrous methylene dichloride. The reaction mixture was heated under reflux for 30 minutes, filtered to remove a solid (A), and cooled.

The mixture was extracted with water, the aqueous layer acidified and the organic extract dried over anhydrous magnesium sulphate. The solvent was removed yielding a dark red tar, which on trituration with benzene/methanol produced a yellow solid (0.16g). The t.l.c. showed a fast moving yellow spot (silica/benzene) so the compound was chromatographed on activated alumina to give a yellow solid (0.11g).

Mass Spectrum:  $m/e$  (% abundance): 334 (max peak of 4×Cl pattern, 50%); (330 max peak of 4×Cl pattern, 50%); 300 (max peak of 4×Cl pattern, 100%); 266 (50%); 264 (50%); 256 (50%); 230 (max peak of 4Cl pattern, 25%).

The product (A) obtained after filtration was identified as a mixture of naphthalene-1,5-dithiol and sulphur.

The Reaction of Naphthalene-1,5-dithiol with Thionyl Chloride

Naphthalene-1,5-dithiol (0.96g, 0.005 mol) and thionyl chloride (5 ml) were heated under reflux for 1 minute after which time the mixture became solid. The solid was removed and dried in a vacuum desiccator to give a yellow solid (1.0g).

Infra-red Spectrum: poorly defined:  $\nu$   $\text{cm}^{-1}$ ; 2900 (S), 1590 (W), 1330 (W), 1220 (W), 1160 (W), 790 (S), 730 (M).

Mass Spectrum:  $m/e$  (% abundance); 478 (3%), 476 (6%); 446 (30%), 444 (100%); 414 (6%); 412 (25%); 382 (25%); 380 (30%); 223 (20%); 221 (100%); 192 (100%); 190 (90%); 160 (40%); 159 (40%) obtained at 260°.

Exact Mass Measurements:

|                     |  |
|---------------------|--|
| $M^+$ , 443 . 92568 | $C_{20}H_{12}S_6$ requires 443 . 92633 |
| $M^+$ , 475 . 90154 | $C_{20}H_{12}S_7$ requires 475 . 89840 |

COMPOUNDS CONTAINING AN ACENAPHTHYLENE NUCLEUS

The Preparation of 5,6-Dichloroacenaphthene

a) Without a catalyst

Acenaphthene (30.8g, 0.2 mol) was dissolved in the minimum volume of cold, dry chloroform, and sulphuryl chloride (46 ml, 76.8g, 0.57 mol) was added slowly. The solution turned reddish-brown and hydrogen chloride was evolved. The apparatus was protected by a calcium chloride guard tube, and left for five days. The deposit was filtered off and recrystallised from methanol. (2.6g, 6%, m.p. 158-159°C, lit m.p. 159-160°C).<sup>(81)</sup>

p.m.r. (CDCl<sub>3</sub>),  $\tau$  : 2.52 (d, 2H, J = 7Hz, Ar.H); 2.87 (d, 2H, J = 7Hz, Ar.H); 6.70 (s, 4H, Ar.CH<sub>2</sub>-CH<sub>2</sub>.Ar).

b) Using Anhydrous Ferric Chloride as Catalyst

Acenaphthene (15.4g, 0.1 mol) was dissolved in ice-cold, dry chloroform, and anhydrous ferric chloride (3.25g, 0.02 mol), and sulphuryl chloride (24.4 ml, 40.5g, 0.3 mol) were added slowly. The solution was protected by a calcium chloride drying tube and left in the dark for two days. The volatile components were removed and the brown residue was washed with water, extracted into chloroform and dried. The chloroform was removed in vacuo and the product further purified by continuous Soxhlet extraction into ethanol. The infrared and proton magnetic resonance spectra were identical with those of the foregoing specimen.

Yield = 8.0g (36%) m.p. 158-159°C (lit 159 - 160°C).<sup>(81)</sup>

c) Using Anhydrous Aluminium Chloride as Catalyst

Acenaphthene (30.8g, 0.2 mol) was dissolved in dry chloroform, sulphuryl chloride (48.8 ml, 91.0g, 0.6 mol) was added, and the solution was cooled in ice. Anhydrous aluminium chloride (2.6g, 0.02 mol) was added and, after 30 minutes, the solution had solidified. The product was filtered off, washed with water, dried, and recrystallised from ethanol. The infra-red and p.m.r. spectra were identical with those obtained from the previous specimens.

Yield = 65%. m.p. = 158-159°C (lit 159-160°C).<sup>(81)</sup>

Analysis:

Found : C, 64.3; H, 3.5%

Calc for  $C_{12}H_8Cl_2$ : C, 64.6; H, 3.6%.

The Preparation of 1-Bromo-5,6-dichloroacenaphthene

N-Bromosuccinimide (6.4g, 0.036 mol), which had been recrystallised from boiling water, and 5,6-dichloroacenaphthene (8.0g, 0.036 mol), were dissolved in dry carbon tetrachloride (120 ml). Benzoyl peroxide (0.28g, 0.001 mol) was added and the solution was heated under reflux for 20 minutes. On cooling, a colourless solid was deposited (3.47g) and this was filtered off. (m.p. 122-124°C) The infra-red spectrum was identical with that of succinimide.<sup>(117)</sup> (lit m.p. 124-126°C).<sup>(118)</sup>

The filtrate was evaporated to yield a brown oily solid (10.3g) which was triturated with acetone/ether, and recrystallised from ethanol (yield 6.3g; 58%) m.p. 125-126°C (mixed m.p. with succinimide 110-115°C).

p.m.r. Spectrum: ( $CDCl_3$ ),  $\tau$  : 2.36 - 2.97 (m, 4H, Ar H);

4.22 (d,d, J = 3Hz,  $R.CH_2 - \underline{CH}.Br.R$ ); 5.72-6.50 (m, 2H,  $Ph.\underline{CH}_2.CHBr.R$ ).

Analysis:

Found : C, 47.9; H, 2.4%

$C_{12}H_7BrCl_2$  requires: C, 47.7; H, 2.3%.

The Preparation of 5,6-Dichloroacenaphthylene

a) Using 2,4,6-Collidine

1-Bromo-5,6-dichloroacenaphthene (3.02g, 0.01 mol) and 2,4,6-collidine (25 ml) were heated under reflux for 30 mins. A solid (1.9g) was deposited which was water soluble and gave a yellow precipitate with acidified silver nitrate solution. The solid was filtered off and the filtrate was acidified with aqueous hydrochloric acid and extracted with chloroform. The extract was washed three times with hydrochloric acid (2N), and once with saturated sodium chloride solution, dried, and evaporated in vacuo, to yield an oily solid. Chromatography on 10% deactivated alumina in light petroleum b.p. 40-60°C gave two fractions:-

- 1) A yellow-orange band which yielded yellow-orange crystals (0.51g). The physical data were consistent with the required product (see below) (yield, 23%).
- 2) A brown band which yielded a brown solid (0.15g),  $m/e$  440.

b) Using N,N-Diisopropylethylamine

1-Bromo-5,6-dichloroacenaphthene (0.5g, 0.017 mol) was dissolved in the minimum volume of "Analar" xylene and N,N-diisopropylethylamine (0.22g, 0.017 mol) added. The solution was heated under reflux for 1 h and a solid (0.20g) was filtered off. This solid formed a yellow precipitate with acidified silver nitrate solution. The remaining solution was washed several times with hydrochloric acid (2N) and water, dried, and the xylene removed in



vacuo. The resulting oily solid was chromatographed on 10% deactivated alumina (light petroleum b.p. 40-60°C) and recrystallised from ethanol (yield, 0.24g; 66%) m.p. 153-156°C.

Analysis:

Found : C, 64.7; H, 2.8%

$C_{12}H_6Cl_2$  requires: C, 65.0; H, 2.7%.

p.m.r. Spectrum: ( $CDCl_3$ ),  $\tau$  : 2.50 (d, 4H,  $J = 1.2\text{Hz}$ , Ar H);

3.1 (s, 2H, Ar.CH = CH - Ar).

Mass Spectrum:  $m/e$  (% abundance): 224 (P+4, 10%); 222 (P+2, 65%); 220 (P, 100%); 189 (1%); 187 (6%); 185 (10%); 150 (13%); 111 (8%); 110 (12%).

$m^*$  : 156 (220  $\rightarrow$  185)

The Attempted Preparation of Acenaphtho[5,6-cd] 1,2-dithiole from 5,6-Dichloroacenaphthylene

a) With Sodium Sulphide Nonahydrate

5,6-Dichloroacenaphthylene (0.22g, 0.01 mol) was dissolved in cold N,N-dimethylformamide, and a solution of sodium sulphide nonahydrate (0.72g, 0.03 mol) in water, added. A precipitate of starting materials formed, but redissolved on heating. The solution was heated under reflux for 3 h and on cooling a brown solid formed. The mixture was diluted with water and extracted several times with methylene dichloride. The combined organic extract was dried over anhydrous magnesium sulphate and the solvent was removed under vacuum to yield a brown solid (0.02g), the infra-red and mass spectra of which were identical with those of 5,6-dichloroacenaphthylene.

The aqueous layer was treated with hydrochloric acid (2N), forming a brown suspension from which a yellow oily solid (0.14g) was



obtained by extraction with ether. The mass spectrum showed 5,6-dichloroacenaphthylene ( $m/e$  220; 100%) to be the predominant product but there was also a sulphur-containing peak at  $m/e$  214 (5%) which could have been due to the required disulphide. Continued heating of the sample did not increase the abundance of the peak and after a short time the peak disappeared. The experiment was repeated on the same scale, with an increased time of reflux (8 h) and worked up in the same way, to give 0.10g of an oily solid. The temperature dependence of the mass spectrum showed that this was probably a mixture of products which did not include the required disulphide:

at 150°C  $m/e$ , 229 (60%); 220 (100%);

at 170°C. 263 (15%); 236 (35%); 234 (100%); 230 (65%); 220 (65%);

202 (60%); 171 (50%).

b) With Anhydrous Sodium Sulphide

Sodium ethoxide was prepared by dissolving finely cut sodium (1g) in absolute ethanol. The solution was halved (A & B) and solution (A) was saturated with hydrogen sulphide gas to form sodium hydrogen sulphide. The remaining solution (B) was then added to the solution of sodium hydrogen sulphide to form sodium sulphide. The product was obtained by precipitation with dry ether (1.7g).

5,6-Dichloroacenaphthylene (0.50g, 0.0028 mol), dry N,N-dimethylformamide, and anhydrous sodium sulphide (from 1g sodium) were heated under reflux for 20 h, cooled and partitioned between water and methylene dichloride. An insoluble solid (0.20g) was filtered off, dried, and a mass spectrum obtained:

$m/e$  (% abundance): 458 (P+2, 25%); 456 (P, 100%); 425 (10%);

230 (10%); 228 (35%); 184 (12%).

The organic extract was dried and evaporated in vacuo to yield an oily solid which was chromatographed on activated alumina to give two fractions:

- 1) 0.16g - starting material, (mass spectrum showed trace of peak  $m/e$ , 214).
- 2) 0.015g of unidentified product.
- c) With Cuprous n-butyl mercaptide <sup>(119)</sup>

5,6-Dichloroacenaphthylene (0.55g, 0.0025 mol), quinoline (12.5 ml) and pyridine (4 ml), were placed in a 3-necked flask fitted with a reflux condenser, a mechanical stirrer, and a thermometer. Cuprous n-butyl mercaptide (0.85g, 0.0055 mol) was added and the solution was stirred and heated under reflux for 4 h. The mixture was allowed to cool to approx 100°C and poured into a stirred mixture of ice (22g) and concentrated hydrochloric acid (6.0 ml). This mixture was stirred occasionally over a period of 2 h and then extracted with ether. The ether extract was filtered, to yield a gold coloured solid (0.60g), (CuSBu) dried, and evaporated to yield a yellow material (0.21g) which appeared to be a mixture of starting material, elemental sulphur and an unidentified minor product.

mass spectrum of gold compound  $m/e$  (% abundance)

180 (5%); 179 (5%); 178 (60%); 147 (10%); 146 (100%); 122 (40%);  
117 (15%); 103 (10%); 87-92 (multiplet, 90-100%).

mass spectrum of yellow material: a) at 150°C: 256, 220/222 and

fragment peaks from these.

b) at 230°C: 322 (P+2, 25%);

321 (P+1, 20%); 320 (P, 100%); 278 (10%) 276 (60%); 273 (10%);  
271 (40%).

### SECTION 3

#### COMPOUNDS CONTAINING A XANTHENE OR THIOXANTHENE NUCLEUS

##### The Preparation of 2,2',6,6'-Tetrachlorobenzil

2,6-Dichlorobenzaldehyde (35g, 0.2 mol), ethanol (80 ml), potassium cyanide (10g, 0.15 mol), and water (50 ml) were heated under reflux for 1.5 h. Water was added to the reaction mixture and the orange solid which precipitated was filtered off, dried, and recrystallised from ethanol as yellow prisms (14.0g, m.p. 226-228°C). The filtrate was extracted several times with ether, the extract was dried and evaporated, and the residue was recrystallised from ethanol to yield a further small amount (1.4g) of the same product. Total yield = 15.4g, 44%.

P.m.r. Spectrum ( $\text{CDCl}_3$ ),  $\tau$  : 2.53 (s, Ar H)

Mass Spectrum:  $m/e$  (% abundance); 177 (P+4, 50%); 175 (P+2, 100%); 173 (P, 80%); 113 (5%); 111 (15%); 109 (5%); 75 (20%).

##### Analysis

Found : C, 48.2; H, 1.7%

$\text{C}_{14}\text{H}_6\text{Cl}_4\text{O}_2$ : C, 48.3; H, 1.7%.

##### The Preparation of 2,2',6,6'-Tetrachlorobenzilic acid

2,2',6,6'-Tetrachlorobenzil (4.0g, 0.0175 mol) was dissolved in the minimum amount of ethanol at 30-40°C and an aqueous solution of potassium hydroxide (2.6g, 0.05 mol) was added. The solution was heated under reflux for 30 min, and kept for 2 days before being poured into water and extracted several times with chloroform. The aqueous extracts were acidified and the product extracted into chloroform. Evaporation of the dried chloroform solution, and recrystallisation of the residue from benzene gave the product

(3.14g, 75%) m.p. 119-121°C as colourless prisms.

Infra-red Spectrum:  $\nu_{\max}$  3500 (OH), 3200 (OH), 1700 (C=O)  $\text{cm}^{-1}$ .

P.m.r. Spectrum  $\{(\text{CD}_3)_2\text{CO}\}$ ,  $\tau$  : 2.70 (m, 6H, Ar H), 1.8-3.2 (v. broad, 2H - OH and  $\text{CO}_2\text{H}$ ).

Mass Spectrum:  $m/e$  (% abundance): 370-364 (q, 366 max >1%);

325 (20%); 323 (40%); 321 (75%); 319 (60%); 302 (q, 304 max, 7%);

290-283 (m, 285 max, 5%); 271 (2%); 269 (7%); 267 (7%); 177 (10%);

175 (70%); 173 (100%); 147 (9%); 145 (10%); 139 (10%); 137 (5%);

111 (10%); 110 (9%); 109 (9%).

$m^*$  282 (366→321); 238 (304→269); 121 (173→145); 93 (321→173).

#### Analysis

Found : C, 45.7; H, 2.0%

$\text{C}_{14}\text{H}_8\text{Cl}_4\text{O}_3$  requires: C, 45.8; H, 2.2%.

#### The Preparation of 2,2',6,6'-Tetrachlorobenzophenone

2,2',6,6'-Tetrachlorobenzilic acid (0.15g, 0.0004 mol) was dissolved in "Analar" acetic acid, and a solution of chromium trioxide in "Analar" acetic acid, added. The solution was heated under reflux for 5 h by which time a complete colour change from maroon to green had occurred. The acetic acid was removed, in vacuo, water was added to the residue, and the resulting solid was filtered off. The product was dried and recrystallised from ethanol to yield colourless needles (0.10g, 84%) m.p. 193-194°C.

P.m.r. Spectrum ( $\text{CDCl}_3$ ),  $\tau$  : 2.71 (s, Ar H)

Mass Spectrum  $m/e$  (% abundance): 324 (5%); 322 (12%); 320 (25%);

318 (17%); 283-287 (t, 285, >1%); 248-252 (t, 248 >1%); 220-224

(t, 220, >1%); 177 (10%); 175 (65%); 173 (100%); 147 (6%); 145 (10%);

111 (4%); 109 (8%).

m\*; 121 (173→145); 93 (320→173).

### Analysis

Found : C, 48.5; H, 1.9%

$C_{13}H_6Cl_4O$  requires: C, 48.7; H, 1.9%.

### The Reaction of 2,2',6,6'-Tetrachlorobenzophenone with Sodium Sulphide Nonahydrate

2,2',6,6'-Tetrachlorobenzophenone (1.6g, 0.005 mol) was dissolved in N,N-dimethylformamide, and a solution of sodium sulphide nonahydrate (7.2g, 0.030 mol) in N,N-dimethylformamide (blue solution) was added. The solution was heated under reflux for 2 h during which several colour changes occurred (blue → green → purple → red). The reaction was cooled and a colourless solid (1.3g) was filtered off. This appeared to be mainly sodium chloride since it was soluble in water and gave a positive test for chloride ion ( $AgNO_3 - HNO_3$ ). The filtrate was diluted with water and extracted with chloroform and the extract was washed several times with water, dried, and evaporated to yield a green solid (0.81g). This was redissolved in the minimum volume of chloroform and chromatographed on activated alumina to give two fractions:-

- 1) a purple band (eluted with benzene) which yielded a purple solid. Recrystallisation from 1,1,2-trichloroethane gave purple-red needles (0.23g, 16%) m.p. 305-308°C.

P.m.r. Spectrum ( $CS_2$ ),  $\tau$  : 2.74 (dd,  $\underline{J}$  = 1.6, Hz. 7.8, Hz. 2H, H-2) 2.98 (dd,  $\underline{J}$  = 7.4, Hz, 7.8 Hz, 2H, H-3); 3.17 (dd,  $\underline{J}$  = 1.6Hz, 7.4, Hz, 2H, H-4).

Because of the low solubility of the compound, the p.m.r. spectrum was obtained by the pulsed Fourier transform technique using a Varian

XL100 NMR Spectrometer.

Mass Spectrum  $m/e$  (% abundance); 292 (P+2, 20%); 291 (P+1, 15%); 290 (P, 100%); 260 (>1%); 258 (4%); 248 (2%); 246 (20%); 147 (2%); 145 (10%); 125 (4%); 123 (20%).

$m^*$  : 208.6 (290  $\rightarrow$  246).

Analysis:

Found : C, 53.5; H, 1.9%

$C_{13}H_6S_4$  requires: C, 53.8; H, 2.1%.

- 2) a yellow band (eluted with methanol) which yielded a yellow-green solid (0.50g) (after recrystallisation from 1,1,2-trichloroethane).

Analysis:

Found : C, 59.15; H, 2.75%

A sample of this product was sublimed (280°C, 0.1 mm Hg) to yield a small amount of purple solid which proved to be identical with that obtained from band 1.

Another sample of the yellow-green product was heated under reflux with benzene for 8 h during which the solvent slowly became purple. Evaporation of the solvent yielded a purple compound whose infra-red and mass spectra were identical with those from the product of fraction 1.

Attempted Reaction of Thioxanthone with Thallium trifluoroacetate followed by Potassium iodide (an application of the method of A. McKillop and E.C. Taylor) (120)

- a) Thioxanthone (0.21g, 0.001 mol), was dissolved in trifluoroacetic acid (10 ml) and thallium (III) trifluoroacetate (0.54g, 0.001 mol) added, taking precautions due to the toxic hazard of this compound.

The mixture was stirred for 48 h and an aqueous solution of potassium iodide (0.38g, 0.023 mol) was added. Stirring was continued for 15 minutes, sodium metabisulphite added, and stirring continued for a further 15 minutes. The solution was basified with NaOH (4N), diluted with ether, and the yellow thallium iodide filtered off. The organic extract was dried and evaporated to yield a yellow solid (0.18g). This was shown by mass spectroscopy and infra-red spectroscopy to be thioxanthone.

b) Thioxanthone (0.21g, 0.001 mol), acetonitrile (10 ml), and thallium (III) trifluoroacetate (0.54g, 0.001 mol) were heated under reflux for 8 h and an aqueous solution of potassium iodide added. The reaction was worked up as above, to give thioxanthone (0.19g) characterised by its mass spectrum, infra-red spectrum and m.p. (208 - 209°C).

#### The Reaction of Thioxanthone with Mercuric Acetate

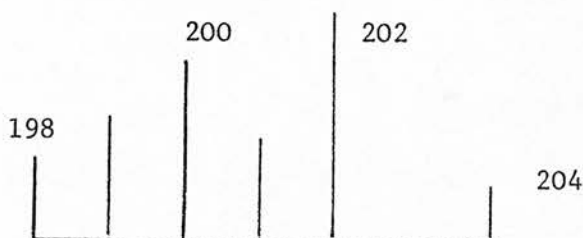
##### a) Using Trifluoroacetic acid as solvent

Thioxanthone (0.21g, 0.001 mol), trifluoroacetic acid (10 ml) and mercuric acetate (0.32g, 0.001 mol) were stirred together for 48 h and an aqueous solution of sodium chloride (1g) was added. The yellow precipitate, which formed immediately, was removed, washed with hot chloroform (to remove unreacted thioxanthone) dried and recrystallised from 1,2,4-trichlorobenzene, to give a mono(chloro-mercuri)-derivative (0.30g; 66%) m.p. (306 - 311°C).

When the experiment was repeated, with stirring for 72 h an almost quantitative yield (0.44g) was obtained.



Mass Spectrum:  $m/e$  (% abundance). The  $m/e$  values quoted for ions containing mercury are those corresponding to the mercury isotope ( $^{202}\text{Hg}$ ) and chlorine isotope ( $^{35}\text{Cl}$ ) of highest natural abundance.



448 ( $^{202}\text{Hg}$ , 100%); 420 ( $^{202}\text{Hg}$ , <1%); 413 ( $^{202}\text{Hg}$ , <1%); 272 ( $^{202}\text{Hg}$ , 5%); 211 (50%); 183 (30%); 139 (60%).

$m^+$ : 394 (448  $\rightarrow$  420); 380 (448  $\rightarrow$  413); 159 (211  $\rightarrow$  183); 105 (183  $\rightarrow$  139); 99 (448  $\rightarrow$  211).

b) Using Acetic Acid as solvent

Thioxanthone (0.21g, 0.001 mol), mercuric acetate (0.32g, 0.001 mol) and acetic acid (15 ml) were heated under reflux for 6 h, and cooled. Aqueous sodium chloride (1g) solution was added and the precipitate which formed was washed several times with water and dried. Mass spectroscopic analysis showed the product to contain only thioxanthone - (0.19g).  $m.p.$  =  $209^{\circ}\text{C}$

c) Using Trifluoroacetic acid as Solvent with a 2 Molar Ratio of Mercuric acetate over Thioxanthone

Thioxanthone (2.12g, 0.01 mol), trifluoroacetic acid (25 ml) and mercuric acetate (6.36g, 0.02 mol) were stirred continuously for 4 days and an aqueous sodium chloride (10g NaCl) solution was



added. The mixture was warmed and stirred for a further hour. The resulting yellow solid (6.15g) was filtered off, washed with water and then with benzene, and dried. Recrystallisation from 1,2,4-trichlorobenzene gave the product as yellow crystals (4.2g). Mass spectroscopic analysis showed the product to be the mono (chloro-mercuri)-derivative  $m/e$ , 448 [ $^{202}\text{Hg}$ ]. m.p. = 306 - 311°C

#### The Reaction of the Chloromercurithioxanthone with Bromine

The chloromercuri-compound (0.22g, 0.005 mol), which had been recrystallised from 1,2,4-trichlorobenzene, and then from o-dichlorobenzene, was suspended in dry chloroform (10 ml). Bromine (0.08g, 0.005 mol) was added, the reaction mixture was stirred for 15 h at room temperature and then gently heated until the bromine colour was finally dispelled. The solution was filtered and the clear filtrate evaporated, in vacuo, to yield a red-brown solid.

This solid was dissolved in N,N-dimethylformamide and treated with sodium sulphide nonahydrate (1g) to destroy any mercuric halides which might have been present. The solution was diluted with water, the product extracted into chloroform, and the extract washed with water. The extract was dried over anhydrous magnesium sulphate and evaporated in vacuo to yield a yellow solid (0.14g).

Infra-red Spectrum:  $\nu$ ,  $\text{cm}^{-1}$ , (Nujol): 2850-3000 (BS), 1680 (S), 1590 (M), 1580 (M), 1315 (M), 1290 (W), 1260 (W), 1160 (W), 1120 (W), 1035 (W), 950 (W), 905 (W), 810 (S), 780 (M), 740 (S), 670 (M).

Mass Spectrum:  $m/e$ , (% abundance); 368, 370, 372 (1:2:1, t, <1%); 292 (P, 100%); 290 (P, 100%); 264 (10%); 262 (10%); 212 (20%); 183 (15%); 149 (20%); 139 (25%); 91 (10%). ( $\text{C}_{13}\text{H}_7^{79}\text{BrOS}$  requires P = 290).

$m^*$  : 240 (290  $\rightarrow$  262); 237 (292  $\rightarrow$  264); 153 (290  $\rightarrow$  211);  
159 (211  $\rightarrow$  183); 127 (264  $\rightarrow$  183).

P.m.r. Spectrum ( $CDCl_3$ ),  $\tau$  : 1.34 - 1.60 (m, 1H, ArH); 2.12 - 2.70 (m, 6H, Ar-H). This spectrum was obtained from a sample which had been repeatedly chromatographed on activated alumina to remove the dibromo-derivative (1,7-?) present as an impurity.

#### The Reaction of the Chloromercurithioxanthone with Mercuric Acetate

The complex (0.11g, 0.00025 mol), mercuric acetate (0.08g, 0.00025 mol) and trifluoroacetic acid (20 ml) were heated under reflux for 24 h.

An aqueous solution of sodium chloride (0.25g) was added and the reaction mixture stirred continuously for 2 h. The solid product was filtered off and dried in a vacuum desiccator (0.08g). Mass spectroscopic analysis showed the solid to be the mono-(chloromercuri)-compound. m.p. = 304 - 310°C

#### The Reaction of Xanthone with Mercuric Acetate

##### a) In Trifluoroacetic acid

Xanthone (1.96g, 0.01 mol), trifluoroacetic acid (20 ml) and mercuric acetate (3.18g, 0.01 mol) were warmed together to effect complete solution, and stirred continuously for 72 h. An aqueous solution of sodium chloride (10g) was added, and the reaction mixture stirred for a further 2 h. The solid which appeared, was filtered off, dried, and purified by Soxhlet extraction with boiling chloroform. (Xanthone is soluble in hot chloroform). Recrystallisation from o-dichlorobenzene gave the product as white crystals (4.0g; 93%)  
m.p.. >340°C

Mass Spectrum:  $m/e$ , (% abundance): 432 ( $^{202}\text{Hg}$ , 70%); 404 ( $^{202}\text{Hg}$ , 2%); 397 ( $^{202}\text{Hg}$ , 5%); 362 ( $^{202}\text{Hg}$ , 2%); 316 ( $^{202}\text{Hg}$ , 4%); 272 ( $^{202}\text{Hg}$ , 20%); 196 (100%); 195 (60%); 168 (90%); 139 (90%).

( $\text{C}_{13}\text{H}_7\text{O}_2$   $^{202}\text{Hg}$   $^{35}\text{Cl}$  requires  $P = 432$ ).

$m^*$  378 (432  $\rightarrow$  404); 365 (432  $\rightarrow$  397); 144 (195  $\rightarrow$  167).

b) In Acetic acid

The above experiment was repeated using the same quantities of reactants. Acetic acid was used (50 ml) as solvent and the reaction mixture was heated under reflux for 24 h and worked up as above. Starting material was recovered.

PREPARATION OF COMPOUNDS CONTAINING AN ANTHRACENE NUCLEUS

The Reaction of 1,8-Dichloro-4,5-dinitroanthraquinone with Sodium Sulphide Nonahydrate

A solution of sodium sulphide nonahydrate (10.8g, 0.045 mol), in N,N-dimethylformamide (50 ml) and water (50 ml), was added to a solution of 1,8-dichloro-4,5-dinitroanthraquinone (1.85g, 0.005 mol) in N,N-dimethylformamide (100 ml) and the mixture was heated under reflux for 5 h. The original blue solution immediately turned green and a solid was slowly deposited over the period of reflux. The green solid (1.58g) was filtered off, washed with water and acetone, and finally dried. The product was further purified by Soxhlet extraction with acetone, the pure compound remaining in the thimble.

Infra-red Spectrum:  $\nu_{\max}$ , 3370 (NH), 1620 (C=O)  $\text{cm}^{-1}$

m.p.  $>325^{\circ}\text{C}$

Mass Spectrum:  $m/e$  (% abundance): 364 (1%); 332 (1%); 318 (P+2, 10%); 316 (P, 100%); 272 (5%); 158 (12%); 136 (3%).

$m^*$  234 (316  $\rightarrow$  272)

exact mass measurement  $M^+$ , 315.97958 ( $\text{C}_{14}\text{H}_8\text{N}_2\text{OS}_3$  requires  $M^+$ , 315.97988).

Analysis:

Found : C, 53.0; H, 2.5; N, 8.7; S, 30.5%

$\text{C}_{12}\text{H}_8\text{N}_2\text{OS}_3$  requires: C, 53.2; H, 2.5; N, 8.9; S, 30.4%.

The Reaction of 1,4,5,8-Tetrachloroanthraquinone with Sodium Sulphide Nonahydrate

A modification of the method used by S. Davidson.<sup>(29)</sup>

1,4,5,8-Tetrachloroanthraquinone (5.7g, 0.016 mol), which had been recrystallised three times from chlorobenzene, was dissolved in redistilled N,N-dimethylformamide and a saturated solution of "Analar" sodium sulphide nonahydrate (42g, 0.175 mol) in N,N-dimethylformamide - water (1:1) was added. The reaction mixture was heated under reflux for 8 h, cooled, and a green solid with a metallic lustre (2.2g) filtered off. This solid had been slowly deposited over the course of the reaction.

Soxhlet extraction of the green product with N,N-dimethylformamide for 24 h removed some impurities and the solid remaining in the thimble was further extracted for 3 days with 1,2,4-trichlorobenzene. The solid which crystallised from the solvent (A, 0.2g) and the solid remaining in the thimble (B, 0.9g) were washed with acetone and submitted for analysis. m.p. >325°C.

Analysis:

Found : (A) C, 45.0; H, 1.2%

Found : (B) C, 46.8; H, 1.2%.

$C_{12}H_4S_6$  requires: C, 46.2; H, 1.1; S, 52.7%,

The two solids were further purified by Soxhlet extraction with acetone for seven days to yield anthra(1,9,8-b c d e : 5,10,4-b'c'd'e')bis thiathiophthen of satisfactory purity.

Analysis:

Found : (A) C, 46.3; H, 1.1%

Found : (B) C, 46.1; H, 1.2; S, 51.9%.

Mass Spectrum:  $m/e$  (% abundance): 366 (P+2, 25%); 364 (P, 100%); 322 (2%); 320 (10%); 182 (25%).  
 $m^*$  283 (364  $\rightarrow$  320).

The filtrate from the original reaction mixture was diluted with water and acidified with dilute hydrochloric acid (2N) to form a black solid which was filtered off (3.3g).

Mass Spectrum:  $m/e$  (% abundance): 330 (P, 60%,  $^{35}\text{Cl}_4$ ); 328 (30%); 295 (100%  $^{35}\text{Cl}_3$ ); 267 (10%); 260 (20%); 231 (20%); 197 (10%); 166 (10%); 165 (10%); 161 (10%).

Exact mass measurements:  $M^+$ , 329.92016 ( $\text{C}_{14}\text{H}_6\text{O}^{35}\text{Cl}_4$  requires  $M^+$ , 329.91727)

$M^+$ , 331.91518 ( $\text{C}_{14}\text{H}_6\text{O}^{35}\text{Cl}_3^{37}\text{Cl}$  requires  $M^+$ , 331.91432)

$M^+$ , 333.91183 ( $\text{C}_{14}\text{H}_6\text{O}^{35}\text{Cl}_2^{37}\text{Cl}_2$  requires  $M^+$ , 333.91137)

$M^+$ , 335.90946 ( $\text{C}_{14}\text{H}_6\text{O}^{35}\text{Cl}^{37}\text{Cl}_3$  requires  $M^+$ , 335.90842)

$M^+$ , 327.92937 ( $\text{C}_{14}\text{H}_7\text{OS}^{35}\text{Cl}_3$  requires  $M^+$ , 327.92832).

The Reaction of 1,5-Dichloro-4,8-dinitroanthraquinone with Sodium Sulphide Nonahydrate

The anthraquinone (1.35g, 0.05 mol), sodium sulphide nonahydrate (10.8g, 0.045 mol), N,N-dimethylformamide (150 ml) and water (50 ml), were heated under reflux for 20 h. The colour of the reaction mixture changed several times (blue  $\rightarrow$  green  $\rightarrow$  purple  $\rightarrow$  dark red) and a deep purple solid (1.2g) was deposited. This compound was insoluble in organic solvents and involatile in the mass spectrometer.

Analysis:

Found : C, 50.0; H, 2.7; N, 8.5%.

The unidentified substance (0.43g) was dissolved in alkaline sodium dithionite (10g in 150 ml NaOH.{2N}) whereupon immediate colour changes occurred to blue and then to reddish-brown. The solution was treated with dimethyl sulphate (0.46g, 0.37 mol) and stirred vigorously for 3 h when a solid (0.10g) was obtained.

Analysis:

Found : C, 50.2; H, 2.7; N, 8.6; S, 26.9%.

The Preparation of 1,8-Dichloro-9-anthrone

This compound was prepared by the method of E. de B. Barnett and M.A. Matthews,<sup>(95)</sup> by reduction of 1,8-dichloroanthraquinone and powdered aluminium in concentrated sulphuric acid. It was recrystallised from chloroform : light petroleum b.p. 40-60°C (1:1) to give yellow crystals m.p. 166-167°C (lit. 167°C)<sup>(95)</sup>.

P.m.r. (CHCl<sub>3</sub>),  $\tau$  : 2.66 (m, 6H, ArH); 5.87 (s, 2H, Ar-CH<sub>2</sub>-X).

The Reaction of 1,8-Dichloro-9-anthrone with Sodium Sulphide Nonahydrate

a) With N,N-dimethylformamide as solvent

1,8-Dichloro-9-anthrone (0.26g, 0.001 mol) was dissolved in N,N-dimethylformamide (10 ml) and added to a solution of sodium sulphide nonahydrate (0.96g, 0.004 mol) in N,N-dimethylformamide (5 ml) and water (5 ml) whereupon a red colour was immediately produced. The reaction mixture was heated under reflux for 24 h and cooled but no solid was obtained. The solution was poured into water, acidified with dilute hydrochloric acid (2N) and the resulting green solid (0.25g) filtered off. The p.m.r. spectrum obtained from this product was very weak but showed the presence of the starting material. The mass spectrum showed a mixture of starting material



$m/e$  , 262 ( $^{35}\text{Cl}_2$ ) and also  $m/e$  , 276 ( $^{35}\text{Cl}_2$ ) which is the anthraquinone.

b) With ethanol as solvent

The anthrone (0.26g, 0.001 mol), ethanol (20 ml) and a solution of sodium sulphide nonahydrate (0.96g, 0.004 mol) in N,N-dimethylformamide (10 ml) and water (10 ml) were heated under reflux for 8 h. The solution immediately became red and, on cooling, deposited a solid (0.16g) which was filtered off.

Infra-red Spectrum:  $\nu$ , 1690 (C=O)  $\text{cm}^{-1}$ .

Mass Spectrum:  $m/e$  (% abundance): 522 (P, 100%,  $\{^{35}\text{Cl}_3^{37}\text{Cl}\}$  strongest peak of 4Cl pattern); 487 (multiplet of peaks max. 487, 10%); 462-449 (multiplet, 449 max, 8%); 422 (10%); 415 (10%); 393 (10%); 386 (10%); 358 (12%); 322 (15%); 276 (33%); 179 (33%); 161 (60%).  
 $m^*$  454 (522  $\rightarrow$  487), 419 (487  $\rightarrow$  452), 417 (487  $\rightarrow$  450), 383 (450  $\rightarrow$  415), 390 (457  $\rightarrow$  422), 355 (485  $\rightarrow$  415).

The above data suggests the solid is dimeric, formed from two molecules of the anthrone with loss of four hydrogen atoms.

Acidification of the filtrate with hydrochloric acid (2N) precipitated a solid (0.06g), the infra-red spectrum of which was identical with that of 1,8-dichloroanthraquinone. The mass spectrum showed the parent ion at  $m/e$ , 276 ( $^{35}\text{Cl}_2$ ) which confirms that the compound was 1,8-dichloroanthraquinone.

The Preparation of 5-oxo-5H anthra(1,9,8-bcde)thiathiophthen

This compound was prepared by the method of S. Davidson and (29) D Leaver by the action of sodium sulphide nonahydrate on 1,8-dichloroanthraquinone in N,N-dimethylformamide.

m.p. 292 - 294°C (lit. 293-294°C). (29)



Attempted Wolff-Kishner<sup>(121)</sup> Reduction of 5-oxo-5H anthra(1,9,8-bcde)-thiathiophthen

The thiathiophthen (0.28g, 0.001 mol), diethylene glycol (50 ml) potassium hydroxide (1.3g, 0.023 mol) and hydrazine hydrate (1.05 ml, 1.08g, 0.022 mol) were heated under reflux for 1 h. Various colour changes occurred (green → purple → red → orange) and a solid (0.58g) was deposited which was involatile in the mass spectrometer.

This product was resistant to acidification and extraction by common organic solvents.

Reactions of Anthra(1,9,8-bcde:5,10,4-b'c'd'e')bis(thiathiophthen)

A. With Alkaline Sodium Dithionite and Dimethyl Sulphate

i) With a large excess of dithionite

a) In the cold

The hexathioanthracene (0.2g, 0.006 mol), sodium dithionite (0.5g), sodium hydroxide (50 ml of 2N) and dimethyl sulphate (2 ml) were stirred continuously for 24h. A brown solid (0.1g) was deposited and this was filtered off, and washed with chloroform to give:

- 1) a chloroform-soluble product (0.02g) which gave the following mass spectrum

$m/e$  (% abundance): 394 (20%), 379 (20%), 378 (20%), 364 (100%), 348 (10%), 332 (10%), 320 (15%).

- 2) a chloroform-insoluble product (0.08g) which gave the following mass spectrum:

$m/e$  (% abundance): 424 (3%), 408 (1%), 394 (15%), 378 (100%), 362 (60%), 348 (25%), 347 (23%), 332 (25%).

These compounds appear from the mass spectra to be mixtures and were present in such small amounts to render further purification impracticable.

b) With reflux

The hexathioanthracene (0.10g, 0.0003 mol), sodium dithionite (0.25g) and sodium hydroxide (25 ml of 2N) were heated together until a constant colour was obtained in solution. The solution colour changes were green  $\rightarrow$  blue  $\rightarrow$  purple  $\rightarrow$  red  $\rightarrow$  reddish orange. Dimethyl sulphate (1 ml) was added and the solution heated under reflux for 7h. A brown solid (0.105g) was deposited, which was

extracted with chloroform, dried and evaporated to give a solid (0.04g). This was redissolved in a small volume of chloroform, to give a red solution, and chromatographed on activated alumina in toluene and carbon tetrachloride (1:1) to give:

- 1) A pink band which gave an intense crimson solution and, after evaporation, only a trace of residual solid.

Mass Spectrum:  $m/e$  (% abundance): 394 (10%), 379 (100%), 364 (50%), 349 (25%), 334 (25%), 316 (5%), 290 (10%).

Exact Mass Measurements:

|                   |                                      |
|-------------------|--------------------------------------|
| $M^+$ , 393.99518 | $C_{18}H_{18}S_5$ requires 394.00121 |
| $M^+$ , 364.03991 | $C_{18}H_{20}S_4$ requires 364.04478 |

- 2) A yellow band which gave an intense yellow solution from which a brown solid (0.02g) was obtained by evaporation.

Mass Spectrum:  $m/e$  (% abundance): 378 (2%), 362 (100%), 347 (30%), 332 (15%), 317 (15%), 302 (10%).  
 $m^*$  333 (362  $\rightarrow$  347); 318(347  $\rightarrow$  332); 285(347  $\rightarrow$  315).

Exact Mass Measurement:

|                      |                                      |
|----------------------|--------------------------------------|
| $M^+$ , 362.02834    | $C_{18}H_{18}S_4$ requires 362.02913 |
| $C_{16}H_{10}O_2S_4$ | requires 361.95637                   |

The chloroform insoluble fraction (0.06g) was investigated by mass spectroscopy and also recrystallised from ethyl benzoate as yellow plates.

Mass Spectrum:  $m/e$  (% abundance): 378 (1%), 362 (100%), 347 (30%), 332 (5%), 317 (5%), 302 (10%).  
 $m^*$  333(362  $\rightarrow$  347); 318(347  $\rightarrow$  332); 285(347  $\rightarrow$  315).

Analysis:

Found: C, 58.3; H, 5.2%

$C_{18}H_{18}S_4$  requires C, 59.7; H, 5.0%

Sufficient material was available for one recrystallisation only.

ii) Using a one molar ratio of sodium dithionite

The hexathioanthracene (0.10g, 0.0003 mol), sodium dithionite (0.053g, 0.0003 mol), sodium hydroxide (25 ml of 2N) and dimethyl sulphate (0.035g, 0.0003 mol) were heated under reflux for 7h. (T.l.c. showed a purple spot r.f. = 0.7 in toluene/silica, with no starting material spot on the baseline). A purple solid (0.07g) was obtained by filtration.

Mass Spectrum:  $m/e$  (% abundance): 394 (85%), 379 (90%), 364 (100%), 348 (9%), 332 (10%), 320 (12%), 197 (12%), 189 (10%), 182 (30%).

$m^*$  365(394  $\rightarrow$  379), 349(379  $\rightarrow$  364)

Exact Mass Measurement:

$M^+$ , 393.90672 ( $C_{16}H_{10}S_6$  requires 393.91068)

$M^+$ , 363.86497 ( $C_{14}H_4S_6$  requires 363.86373)

B. With Methylfluorosulphonate (magic methyl)

Hexathioanthracene (0.36g, 0.001 mol) and methylfluorosulphonate (10 ml) were heated under reflux for 6 hours. A green solid was deposited (0.50g) which was filtered off, washed with water, extracted with chloroform, dried, and chromatographed on activated alumina to give:

- 1) a purple band which on evaporation of the light petroleum (40-60)/toluene mixture which gave only a trace of residual solid.

Mass Spectrum: 394 (80%), 379 (90%), 364 (100%), 332 (5%), 320 (15%).

- 2) a blue band with pink edges suggesting that two compounds of similar polarity were present.

Mass Spectrum:  $m/e$  (% abundance) 426 (50%), 410 (60%), 394 (70%),  
379 (65%), 364 (100%), 348 (50%), 347 (50%),  
332 (50%), 320 (20%), 314 (20%).

Since there was a possibility of a mixture in this case an H.S.L.C. investigation was undertaken. This showed three major products but only fraction 2 provided sufficient material for a mass spectrum.

$m/e$  (% abundance): 426 (100%), 410 (<5%), 394 (25%), 379 (25%),  
364 (30%), 347 (70%), 332 (25%), 314 (30%).

#### SECTION 4

#### THE PREPARATION OF COMPOUNDS CONTAINING A PYRIDAZINO [4,5-d] PYRIDAZINE NUCLEUS

##### The Preparation of Tetramethyl ethylenetetracarboxylate

The method was an adaptation of that used for the preparation of tetraethyl ethylenetetracarboxylate. (122)

Anhydrous sodium carbonate (20g, 0.19 mol) and dimethyl bromomalonate (26.4g, 0.125 mol) were heated in an open flask, on an oil bath at 150°C for 3 h. Xylene (30 ml), was added to the reaction mixture while it was still hot, the solid cake carefully broken up, and the complete contents of the reaction flask transferred to a large conical flask. The reaction flask was rinsed with a xylene-water mixture (1:1) and these washings added to the conical flask. Water (60 ml) was added to the conical flask, the mixture shaken well and then filtered to give a white solid (10.5g). The product was obtained as white needles from methanol (4.4g, 34%) m.p. 119-120°C.

P.m.r. (CDCl<sub>3</sub>)  $\tau$  : 4.13 (s, -CO<sub>2</sub>CH<sub>3</sub>).

Infra-red Spectrum:  $\nu_{\max}$ , 2800 (CH), 1730 (C=O), 1250, 1040, 1025 (C-O) cm<sup>-1</sup>.

Mass Spectrum:  $m/e$  (% abundance): 260 (P, 10%); 229 (100%); 198 (10%); 173 (5%); 171 (5%); 157 (8%); 140 (5%); 111 (8%).  
 $m^*$  202 (260  $\rightarrow$  229); 176 (230  $\rightarrow$  201); 150 (260  $\rightarrow$  198); 150 (198  $\rightarrow$  173).

##### Preparation of Pyridazino [4,5-d]pyridazine-1,4,5,8-(2H, 3H, 6H, 7H)- tetrone

Tetramethyl ethylenetetracarboxylate (1g, 0.004 mol) was heated with hydrazine hydrate (0.4g, 0.008 mol) at 100°C for 1 h.

The pyridazinopyridazine was obtained as an orange solid which was washed with methanol and dried. Yield 0.64g (86%).

m.p.  $>340^{\circ}\text{C}$  (lit m.p.  $>340^{\circ}\text{C}$ ).

Infra-red Spectrum:  $\nu_{\text{max}}$ , 3500 (BS, NH), 2800 (CH), 1700 (BS, C=O).

Mass Spectrum:  $m/e$  (% abundance): 196 (100%); 167 (75%); 111 (85%).

$m^*$  142 (196  $\rightarrow$  167).

The Reaction of Pyridazino[4,5-d]pyridazine-1,4,5,8-(2H, 3H, 6H, 7H)-tetrone with Phosphorus Pentasulphide

a) With Sulpholane as solvent

The tetrone (0.90g, 0.005 mol), sulpholane (50 ml) and phosphorus pentasulphide (6.1g, 0.028 mol) were heated under reflux for 4 h. The dark brown solution was cooled, poured into water, and extracted with chloroform. The chloroform extract was washed several times with water and dried over anhydrous magnesium sulphate. The chloroform was removed to leave a small amount of an oily solid which was not identified.

b) With Pyridine as solvent

The tetrone (0.90g, 0.005 mol) was dissolved in pyridine, phosphorus pentasulphide (6.1g, 0.028 mol) added, and the reaction mixture heated under reflux for 4 h. The mixture was cooled, poured into water and acidified and the resulting solid (0.8g) was filtered off and dried. The mass spectrum showed this to be starting material contaminated with elemental sulphur.

The Reaction of Pyridazino[4,5-d]pyridazine-1,4,5,8-(2H, 3H, 6H, 7H)-tetrone with phosphorus and sulphur-oxyacid chlorides

a) With Phosphoryl Chloride

The tetrone (0.875g, 0.0045 mol) redistilled phosphoryl chloride (10 ml) and redistilled N,N-diethylaniline (5 ml), were heated under reflux for 2 h (the apparatus being protected by a calcium chloride drying tube). The reaction mixture was allowed to cool slightly and was poured, with continuous stirring onto ice. The solution was filtered, a dark solid (0.24g) removed and dried, and the filtrate extracted with ether. The extract was washed several times with water, dried and evaporated to yield an oil which was



taken up in chloroform and chromatographed on activated alumina. Three fractions were obtained by elution successively with carbon tetrachloride, ether and methanol:

- 1) a yellow band which afforded a brown solid (0.08g),  $m/e = 360$
- 2) a yellow band which afforded an off white solid (0.02g), which was involatile in the mass spectrometer
- 3) a pink band which afforded a brown oily solid (0.01g),  $m/e = 290$

The mass spectra of these products showed that none of them was the required tetrachloropyridazinopyridazine.

b) With Phosphorus pentachloride and Phosphoryl chloride

The tetrone (0.235g, 0.0012 mol), phosphorus pentachloride (1.04g) and freshly distilled phosphoryl chloride (12 ml), were heated together at  $100^{\circ}\text{C}$  for 14 h, the reaction vessel being protected using a  $\text{CaCl}_2$  guard tube. The mixture was filtered to remove a dark oily solid and the residual liquid evaporated and water added to destroy residual phosphoryl chloride. A solid was obtained which was washed with water and dried (0.02g).

Mass Spectrum:  $m/e$  (% abundance): 290 (100%); 275 (100%); 197 (20%).

c) With Sulphuryl chloride

The tetrone (0.50g, 0.025 mol) and sulphuryl chloride (25 ml) were heated under reflux ( $69^{\circ}\text{C}$ ) for 11 h. The apparatus was protected by a calcium chloride guard tube. The solution was filtered and the clear yellow liquid evaporated in vacuo to afford an orange solid (0.45g) the infra-red spectrum of which showed it to be the original tetrone.

d) With Phenylphosphonic dichloride

The tetrone (0.39g, 0.002 mol) and phenylphosphonic dichloride (10 ml) were heated together on an oil bath at 140°C for 7 h, the apparatus being protected by a calcium chloride guard tube. The reaction mixture was added to water, extracted with chloroform and dried over anhydrous magnesium sulphate. A pale yellow solid (0.50g) crystallised out of the aqueous extract whilst the organic layer afforded an oily solid (0.12g). The infra-red and mass spectra of these two samples showed them to be identical.

Mass Spectrum:  $m/e$  (% abundance): 420 (P, 60%); 357 (30%);

327 (15%); 280 (15%); 279 (15%); 263 (18%); 262 (20%); 234 (16%);

216 (100%); 199 (40%); 187 (15%); 158 (60%); 140 (25%).

$m^*$ : 303 (420  $\rightarrow$  357); 195 (357  $\rightarrow$  263); 183 (216  $\rightarrow$  199); 151 (234  $\rightarrow$  187).

$\{(C_6H_5PO_2)_3$  requires P = 420}

Analysis:

Found : C, 47.7; H, 4.2%

$(C_6H_5PO_2)_3$  requires: C, 51; H, 3 %.

## SECTION 5

### PREPARATION OF COMPOUNDS INVOLVED IN INVESTIGATIONS INTO THE REACTION OF ACETYLENES WITH 1,2-DITHIOLE-3-THIONES AND THE REARRANGEMENT OF 2-THIOACYLMETHYLENE-1,3-DITHIOLES TO 1,6,6a-TRITHIAPENTALENES

#### A. The Proposed Spiran Intermediate

##### The Preparation of 2-Methylthio-4-phenyl-1,3-dithiolium Salts

##### a) Perchlorate

This was prepared by the method of E. Campaigne et al.<sup>(105)</sup>

Yield 90%, m.p.  $125\frac{1}{2}$ - $126\frac{1}{2}^{\circ}$  (from ethanol) (lit m.p.  $126$ - $127^{\circ}$ ).

##### b) Bisulphate (Hydrogen Sulphate)

Methyl phenacyl trithiocarbonate (1g, 0.004 mol) was dissolved in 80% sulphuric acid (10 ml) to give a red solution and heated to  $30$ - $40^{\circ}\text{C}$  for 5 minutes. The solution was chilled and diluted with acetic acid (50 ml), ethyl acetate (100 ml), and ether (250 ml), and the product was filtered off. Recrystallisation from ether gave the product as red-brown crystals (0.76g, 54%).

Infra-red Spectrum:  $\nu$ , 1150 (S), 1040 (S), 860 (S) ( $\text{HSO}_4^-$ )  $\text{cm}^{-1}$ .

##### c) Hexafluorophosphate

The trithiocarbonate (1.04g, 0.004 mol) and hexafluorophosphoric acid (10 ml, 65% aqueous) were heated together at  $40^{\circ}$  for five minutes. (Care must be taken because of reaction between HF impurity and the glassware). The reaction mixture deposited crystals on cooling and ethyl acetate was then added to precipitate the remainder of the product. Recrystallisation from ethanol afforded pink crystals (crude yield 1.59g, 100%) m.p.  $161$ - $163^{\circ}$

The infra-red spectrum was essentially the same as that of the perchlorate except for the absence of a strong band at  $1100\text{ cm}^{-1}$  ( $\text{ClO}_4^-$ ) and the presence of one at  $840\text{ cm}^{-1}$  ( $\text{PF}_6^-$ ).

Attempted Demethylation of 2-Methylthio-1,3-dithiolium Salts

a) Using Pyridine

The perchlorate (1g, 0.003 mol) and redistilled pyridine (5 ml) were heated under reflux for 2 h and cooled. The reaction mixture was poured into water (25 ml) and extracted with ether. The ether was concentrated and the product chromatographed on activated alumina. (T.l.c. showed a yellow spot  $r.f. = 0.50$ ) to give a yellow band which produced a brown solid (0.05g), m.p.  $152-154^\circ$ .

Mass Spectrum:  $m/e$  (% abundance): 420 (4%); 419 (4%); 418 (12%); 371 (<1%); 345 (25%); 344 (25%); 343 (100%); 311 (<1%); 279 (15%);  $m^*$ : 282 (418  $\rightarrow$  343).

b) Using Sodium Sulphide Nonahydrate in Ethanol

The dithiolium perchlorate (1g, 0.003 mol) was dissolved in ethanol, sodium sulphide (0.74g, 0.003 mol) added, and the solution heated under reflux for 15 minutes. The original green colour of the solution changed to maroon. The deeply coloured solution was added to water, and extracted several times with ether. The combined ether extracts were dried over anhydrous magnesium sulphate, and the solvent removed in vacuo to afford a red-brown solid which was recrystallised from ethanol to yield 4-phenyl-1,3-dithiole-2-thione (0.16g) as brown needles, m.p.  $117-118^\circ$  (lit m.p.  $117-118^\circ$ ).<sup>(123)</sup>

The infra-red spectrum was identical with that of an authentic sample.

c) Using Sodium Sulphide Nonahydrate in N,N-dimethylformamide

1) With the Perchlorate

Sodium sulphide (0.74g, 0.003 mol), and the dithiolium perchlorate (1.0g, 0.003 mol) were dissolved in the minimum volume of N,N-dimethylformamide and the solution warmed gently for 30 minutes. The reaction mixture was poured into an excess of cold water and extracted several times with ether. The ether was washed several times with water and dried over anhydrous magnesium sulphate. After evaporation of the solvent a maroon solid was obtained (0.37g). This was recrystallised from ethanol to afford the thione as brown-red needles (0.21g), m.p. 116-117°. (lit m.p. 117-118°).<sup>(123)</sup>

2) With the Hexafluorophosphate

The hexafluorophosphate salt (5.5g, 0.015 mol), and sodium sulphide nonahydrate (3.7g, 0.015 mol) were dissolved in the minimum volume of N,N-dimethylformamide and heated under reflux for 45 minutes. The reaction mixture was added to an excess of cold water and extracted several times with ether. The ether was washed several times with water, dried over anhydrous magnesium sulphate and evaporated in vacuo to afford a maroon solid which was recrystallised from ethanol as red-brown needles (0.22g), m.p. 116-117° (lit m.p. 117-118°).<sup>(123)</sup> The infra-red spectrum was identical with that of an authentic sample of 4-phenyl-1,3-dithiole-2-thione.

The Reaction of Sodium Ethoxide with 4-Phenyl-1,3-dithiole-2-thione

(Adaptation of the method used by R. Mayer and B. Gebhardt<sup>(104)</sup> for the preparation of ethylene-1,2-dithiol from 1,3-dithiol-2-one).

4-Phenyl-1,3-dithiole-2-thione (0.50g, 0.0024 mol) was dissolved in absolute alcohol and sodium ethoxide (0.0048 mol; from 0.22g Na) in absolute ethanol was added. The solution was kept under nitrogen for 10 days. Ether was added to precipitate more of the light coloured solid which had been deposited over the period of reaction. The solution was filtered to remove this light coloured solid which was now washed with ether to yield 0.41g, m.p.  $>295^{\circ}\text{C}$ .

A sample of the solid (0.1g) was heated under reflux with thiophosgene, under nitrogen, for 15 minutes, and the thiophosgene removed in vacuo. The solid which remained was triturated with chloroform and the residue (0.075g) was filtered off. T.l.c. of the filtrate showed predominantly thiophosgene with a trace of 4-phenyl-1,3-dithiole-2-thione. Evaporation of the chloroform gave a residue (0.021g) which contained no more than a trace of the thione.

The Preparation of 4-Phenyl-1,3-dithiol-2-one

4-Phenyl-1,3-dithiole-2-thione (1g, 0.005 mol), mercuric acetate (4.6g, 0.015 mol) and acetone (700 ml) were heated under reflux for 30 minutes. The solvent was removed in vacuo and the resulting solid dissolved in a small volume of chloroform and chromatographed on activated alumina in benzene. The yellow product so obtained was recrystallised from ethanol as yellow crystals (0.58g, 63%) m.p.  $93-95^{\circ}\text{C}$  (lit m.p.  $95-96^{\circ}$ ).<sup>(124)</sup>

Mass Spectrum:  $m/e$  (% abundance): 196 (P+2, 8%); 194 (P, 100%); 168 (8%); 166 (65%); 134 (25%); 121 (80%); 102 (70%); 77 (30%);  $M^+$  142 (194  $\rightarrow$  166); 108 (166  $\rightarrow$  134); 89 (166  $\rightarrow$  121); 49 (121  $\rightarrow$  77).

The Reaction of 4-Phenyl-1,3-dithiol-2-one with Sodium Ethoxide

4-Phenyl-1,3-dithiol-2-one (0.50g, 0.0025 mol) was dissolved in absolute ethanol and injected through a rubber serum cap into a nitrogen-flushed flask containing a solution of sodium ethoxide (0.325g, 0.005 mol) in ethanol (20 ml) and the solution was kept for 12 days. The precipitate which formed was filtered off under nitrogen and more solid was obtained by addition of ether to the filtrate (total yield of solid, 0.28g).

Infra-red Spectrum:  $\nu$ ,  $\text{cm}^{-1}$  (Nujol): 3500 (BS); 2900-3000 (S), 1620 (BS); 1360 (M); 1150 (BS); 1100 (M); 1080 (M); 1020 (M); 895 (M); 820 (M); 730 (W); 695 (M).

The Reaction of 4-Phenyl-1,3-dithiol-2-one with Phenyl-lithium

4-Phenyl-1,3-dithiol-2-one (0.54g, 0.0028 mol) was dissolved in sodium-dried ether (20 ml) and added to a solution of phenyl-lithium (prepared from 0.14g of lithium) in sodium-dried ether (10 ml) under a dry nitrogen atmosphere at  $-10^{\circ}\text{C}$ . The solution was stirred for 6 h and the resulting yellow solid (0.60g) filtered off quickly, washed with ether and stored in a vacuum desiccator. The ethereal solution was evaporated and the residual solid was dissolved in a small volume of chloroform and chromatographed on activated alumina to give:-

- 1) a white solid (0.08g)  $m/e$ , 154.
- 2) a yellow solid (0.17g) i.r. identical with starting material.



- 3) a yellow solid (0.30g)  $m_e$ , 260. I.R. spectrum identical with that of an authentic specimen of triphenyl carbinol.

#### Reactions of the foregoing ether-insoluble solid

##### With Thiophosgene

The solid (0.10g) was treated with an excess of thiophosgene (only 50% went into solution) under a nitrogen atmosphere and warmed for 15 minutes. The thiophosgene was removed in vacuo, chloroform was added, and the solution was filtered. A preparative t.l.c. was run on the solution but no 4-phenyl-1,3-dithiole-2-thione was obtained.

#### B. The Effect of Vulcanisation Accelerators in the Sulphur-Catalysed Rearrangement

##### The Preparation of 4-Phenyl-2-thiophenacylidene-1,3-dithiole

5-Phenyl-1,2-dithiole-3-thione (4.2g, 0.02 ml) and phenylpropionic acid (2.9g, 0.02 mol) were dissolved in toluene (200 ml) and heated under reflux for 4 h. The red-brown solution was concentrated and chromatographed on activated alumina to yield the product as a brown solid which was recrystallised as brown flakes from ethyl acetate. (5.4g, 84%) m.p. 199-202° (lit 200-202°).<sup>(26)</sup>

##### The Preparation of some Transition metal dithiocarbamates

General Method: The metal acetate (except in the case of iron when the chloride was used) was dissolved in water and a solution of sodium diethyldithiocarbamate was added. The precipitate which formed was filtered off, dried in a desiccator, and recrystallised several times from chloroform.



Table 1

| Starting Mat   | Reactant                                   | Yield<br>(Purified) |     | m.p.      |          |
|--|--|---------------------|-----|-----------|----------|
|  |  |                     |     | found     | Lit      |
| Co(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> H <sub>2</sub> O<br>(1.25g)  | Na(S-C(=S)-N(Et) <sub>2</sub> )<br>(2.25g) | 1.51g               | 86% | 263-264°C | 263-264° |
| FeCl <sub>3</sub> (2.7g)   | (2.25g)                                    | 1.00g               | 60% | 165-168°C | 167-168° |
| Ni(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> 4H <sub>2</sub> O<br>(1.25g) | (2.25g)                                    | 1.17g               | 67% | 233-236°C | 235-236° |
| Cu(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> H <sub>2</sub> O<br>(1.00g)  | (2.25g)                                    | 1.17g               | 65% | 189-191°C | 189-191° |
| Zn(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> 2H <sub>2</sub> O<br>(1.10g) | (2.25g)                                    | 0.88g               | 50% | 174-177°C |          |

The Rearrangement of 4-Phenyl-2-thiophenacylidene-1,3-dithiole

The 1,3-dithiole (0.1g) was dissolved in xylene or chloro-benzene (12.5 ml) and the catalyst(s) added (sulphur 0.01g, accelerators 0.01g). The solution was heated under reflux until t.l.c. showed the rearrangement to be essentially complete (some of the very slow reactions were stopped before this point was reached). The solution was concentrated, and chromatographed on activated alumina eluting with benzene to give:-

- a red band which yielded the thiathiophthen. B.
- a brown band which yielded starting material. A.

The results are summarised in the table over.

Table 2

| Accelerator (b)   | Solvent | Time (h) | % Yield B | % Recovered A | Mass Accountancy % |
|---|---------|----------|-----------|---------------|--------------------|
| -   | PhCl *  | 100      | 77        | 15            | 92                 |
| -   | (c)     | 75       | 50        | 35            | 98(a)              |
| $\text{Zn}(\text{S}-\overset{\text{S}}{\underset{  }{\text{C}}}-\text{NEt}_2)_2(+)$ | (c)     | 4        | 94        | 0             | 94                 |
| $\text{Cu}(\text{S}-\overset{\text{S}}{\underset{  }{\text{C}}}-\text{NEt}_2)_2(+)$ | (c)     | 26       | 97        | 0             | 97                 |
| $\text{Ni}(\text{S}-\overset{\text{S}}{\underset{  }{\text{C}}}-\text{NEt}_2)_2(-)$ | (c)     | 77       | 90        | 4             | 94                 |
| $\text{Co}(\text{S}-\overset{\text{S}}{\underset{  }{\text{C}}}-\text{NEt}_2)_3(-)$ | (c)     | 31       | 75        | 22            | 97                 |
| $\text{Fe}(\text{S}-\overset{\text{S}}{\underset{  }{\text{C}}}-\text{NEt}_2)_3(+)$ | (c)     | 5        | 95        | 0             | 95                 |
| $\text{Cd}(\text{S}-\overset{\text{S}}{\underset{  }{\text{C}}}-\text{NEt}_2)_2(+)$ | (c)     | 20       | 96        | 0             | 96                 |
| -   | (d)     | 19       | 85        | 10            | 95                 |
| -   | (e)     | 22       | 88        | 8             | 96                 |

\* Purified by washing with concentrated sulphuric acid, drying over anhydrous magnesium sulphate and redistillation.

(a) An addition product (13%) was obtained in this case:  $m/e$  396

(b) The (+) or (-) signs shown are the effects shown by the dithiocarbamates in accelerating the vulcanisation of rubber.

(c) Analar xylene containing high b.p. impurities only.

(d) Sulphur-free xylene containing high and low b.p. impurities.

(e) Sulphur-free xylene containing low b.p. impurities only.

C. The Possible Intermediacy of Thioacylcarbenes in the Reaction of Acetylenes with 1,3-dithiole-3-thiones

The Preparation of 4-(p-Methoxyphenyl)-1,2,3-selenadiazole

(An application of the method of M. Yalpani et al.). (110)

To a stirred suspension of p-methoxyacetophenone semicarbazone (24.2g, 0.11 mol) in 'Analar' acetic acid at room temperature, selenium dioxide (13g, 0.12 mol) was added gradually with cooling. The mixture was stirred for 2 h and filtered to remove deposited selenium. Water was added and the precipitated solid was extracted into chloroform. The extract was washed with aqueous sodium hydrogen carbonate and dried over anhydrous magnesium sulphate. The solvent was evaporated in vacuo to afford the selenadiazole (11.8g; 42%), m.p. 100-101°, (lit m.p. 101°). (125)

The Preparation of p-Methoxyphenylacetylene

(An application of the general method of M. Yalpani). (110)

A mixture of the foregoing selenadiazole (10.5g, 0.07 mol) and acid washed sand (80g) was gradually heated to 160°C and that temperature was maintained for 30 minutes. The reaction vessel was attached to a distillation apparatus and heated under vacuum. This produced p-methoxyphenylacetylene (0.5g) as a yellow liquid which was purified by steam distillation and the structure confirmed by i.r., p.m.r. and mass spectroscopy. Since the yield was low this was not a practical synthetic route to the acetylene. The product used in the reactions below was obtained from p-methoxyacetophenone by the method of S. Davidson, (29) which is a modification of the method of K. Bodendorf and R. Mayer proceeding via 3-chloro-3-(p-methoxyphenyl)prop-2-enal. (126)

Reactions of 5-phenyl-1,2-dithiole-3-thione with p-methoxyphenyl acetylene in Xylene

The thione (0.34g, 0.16 mol) and the acetylene (0.42g, 0.32 mol) were heated together in boiling 'Analar' xylene (12.5 ml) for 3h. The reaction mixture was reduced in volume and chromatographed on alumina. The initial experiment contained no sulphur whereas the second contained an added portion of 0.01g.

Table 3

| Thione | Acetylene | S <sub>8</sub> | Results of Chromatography                    |       | %* |
|--------|-----------|----------------|--|-------|----|
| 0.34g  | 0.42g     | 0              | 1) aryl acetylene                            | 0.25g | 62 |
|        |           |                | 2) thione                                    | 0.21g |    |
|        |           |                | 3) blue band <sup>m</sup> / <sub>e</sub> 288 | 0.01g |    |
|        |           |                | 4) 1,3-adduct                                | 0.18g |    |
| 0.34g  | 0.42g     | 0.01g          | 1) aryl acetylene                            | 0.02g | 28 |
|        |           |                | 2) thiathiophthen                            | 0.16g |    |
|        |           |                | 3) thione                                    | 0.09g |    |
|        |           |                | 4) tar                                       | 0.09g |    |
|        |           |                | 5) 1,3-adduct                                | 0.24g |    |
|        |           |                |  |       | 42 |

\* mass accountancy based on 5-phenyl-1,2-dithiole-3-thione.

The Preparation of 4-Phenyl-1,2,3-thiadiazole

This was prepared by the method of W. Kirmse and L. Horner<sup>(127)</sup> from acetophenone semicarbazone and thionyl chloride.

Yield 70%. m.p. 79-80° (lit<sup>127</sup> m.p. 80-81°).

The Preparation of Phenylacetaldehyde ethoxycarbonylhydrazone

Ethoxycarbonylhydrazine (10.4g, 0.11 mol), freshly distilled phenylacetaldehyde (12.0g, 0.10 mol) and ethanol (100 ml) were left for 2 days, after which time no crystals had appeared. A portion of the mixture was treated dropwise with water until

crystallisation occurred. A few of these crystals were used to seed the main portion and on addition of a few drops of water the mixture crystallised (18.0g). Recrystallisation from aqueous ethanol, and drying in a vacuum desiccator afforded the product as pale yellow crystals (12.5g, 61%), m.p. 92-93°.

Analysis:

Found : C, 63.9; H, 6.7; N, 14.3%

$C_{11}H_{14}N_2O_2$  requires: C, 64.1; H, 6.8; N, 13.6%.

The Preparation of 5-Phenyl-1,2,3-thiadiazole

(a) Phenylacetaldehyde semicarbazone (4.0g, 0.0225 mol) which had been recrystallised to constant melting point, and thionyl chloride (15 ml), were heated under reflux for 2 h. Hydrogen chloride was driven off and excess thionyl chloride removed by distillation. Water was added to the residue, and the resulting dark gum was extracted into chloroform. The extract was dried, and evaporated and the product was purified by chromatography on alumina (5% deactivated) using benzene as eluant. The oil thus obtained, crystallised when seeded with a specimen of the thiadiazole obtained by method (b). Recrystallisation from ethanol gave the product as brown crystals (0.9g, 25%), m.p. 52-52.5° (lit m.p. 53°).<sup>(128)</sup> Vacuum sublimation afforded pale yellow crystals m.p. 53-53.5°C. The i.r. spectrum was identical to that of the product from method (b).

(b) This method was an application of that of W. Kirmse and<sup>(127)</sup> L. Horner. Phenylacetaldehyde ethoxycarbonylhydrazone (5.1g, 0.05 mol), and thionyl chloride (15 ml) were heated under reflux for 2 h. Hydrogen chloride and excess thionyl chloride were distilled off and water added to the resultant oil. The product

was extracted into chloroform and the extract was dried over anhydrous magnesium sulphate and evaporated. The product was purified by chromatography on alumina (5% deactivated) using benzene as eluant. Further purification was carried out by sublimation. Yield 0.52g; 13%. m.p. 52.5-53°, (lit m.p. 53°C).<sup>(128)</sup>

The Reaction of 5-Phenyl-1,2-dithiole-3-thione, with 5-Phenyl-1,2,3-thiadiazole

5-Phenyl-1,2-dithiole-3-thione (0.21g, 0.001 mol) and 5-phenyl-1,2,3-thiadiazole (0.16g, 0.001 mol) were mixed together and heated in a test tube to 200° on an oil bath, for 1½ h. The reaction was monitored by t.l.c. and after 1 h, t.l.c. showed a pink spot corresponding to 2,5-diphenyl-1,6,6a-trithiapentalene (r.f. = 0.60 benzene/silica). After 1½ h the thiadiazole spot had completely disappeared but the spot corresponding to the trithiapentalene was very small and weak relative to that of the original dithiolethione. A further quantity of the thiadiazole (0.5g) was added and heating was continued for 1 h. Chromatography on activated alumina, eluting with light petroleum b.p. 40-60°C: benzene:ether mixtures, gave (i) the trithiapentalene (0.06g), m.p. 160-161°, identical (mixed m.p. and infra-red spectrum) with an authentic specimen, and (ii) the original thione (0.08g).

Thermal Decomposition of 5-Phenyl-1,2,3-thiadiazole and 4-Phenyl-1,2,3-thiadiazole

The thiadiazoles (0.2g) were heated separately at 200°C in an oil bath for 1½ h. The products [(0.1g) of each] were dissolved in ether and investigated by g.l.c. analysis. The chromatograms showed no peaks due to phenylacetylene as a decomposition product.

D. The Effect of Alkyl Substituents in the 1,2-Dithiole-3-thione

The Preparation of 4,5-Dimethyl-1,2-dithiole-3-thione

(The method is based on that of L. Legrand and N. Lozac'h).<sup>(111)</sup>

Ethyl-2-methyl-3-oxobutanoate (20g, 0.14 mol), phosphorus pentasulphide (40g, 0.17 mol), and tetralin (400 ml) were heated under reflux for 40 minutes. After cooling, the reaction mixture was diluted with ether (400 ml), washed with water, sodium hydroxide and water, and dried over anhydrous calcium chloride. A saturated methanolic solution of mercuric chloride (39g) was added to the dry solution and the complex so formed filtered off, washed with ether and dried (32g). The complex was decomposed by shaking for 1 h with a saturated solution of sodium sulphide (slight excess). The mixed solids obtained were washed with water and dried, and the product was extracted into boiling ethanol. Chromatography on alumina (10% deactivated) with benzene as eluant, followed by recrystallisation from methanol, afforded the product as orange-yellow crystals (2.5g, 18%), m.p. 96° (lit m.p. 96°).<sup>(111)</sup>

Reactions of 4,5-Dimethyl-1,2-dithiole-3-thione with Arylacetylenes

a) With Phenylacetylene

The thione (1.0g, 0.0062 mol), phenylacetylene (1.3g, 0.0125 mol) and 'Analar' benzene (30 ml) were heated under reflux, and the reaction monitored by t.l.c. No change was noted after 5 h so heating was discontinued.

The experiment was repeated using the higher boiling solvent chlorobenzene, which had been washed with concentrated sulphuric acid, dried over anhydrous magnesium sulphate and redistilled. The reaction proceeded with no change for 1 h, but after 1.5 h a red spot ( $r_f = 0.6$ , silica/benzene) appeared on the t.l.c. plate in



addition to the starting materials. After 30 h, when the reaction was almost complete, the solution was cooled, concentrated, and chromatographed on activated alumina, eluting with light petroleum/benzene mixtures, to give the following fractions:-

1) a yellow band which on evaporation gave an unidentified oil (0.04g).

Mass Spectrum:  $m/e$  (% abundance): 238 (P+2, 10%); 236 (P, 30%); 204 (15%); 202 (10%); 112 (40%); 102 (100%).

2) a red band which yielded red crystals (0.76g).

Recrystallisation from benzene/ethanol (1:1) afforded 2,3-dimethyl-5-phenyl-1,6,6a-trithiapentalene as red needles (0.57g).

m.p. 149-150<sup>o</sup>, identified from its <sup>1</sup>H n.m.r. spectrum.

Analysis:

Found : C, 59.1; H, 4.6%

C<sub>13</sub>H<sub>12</sub>S<sub>3</sub> requires: C, 59.1; H, 4.4%.

P.m.r.: (CDCl<sub>3</sub>)  $\tau$  : 2.00 (s, 1H, 3-H); 2.12-2.22 (m, 2H, o-Ar-H); 2.58-2.65 (mult, 3H, m-p-Ar-H); 7.47 (s, 3H, -CH<sub>3</sub>); 7.59 (s, 3H, -CH<sub>3</sub>).

3) an orange band which yielded the original thione (0.19g).

4) a brown band which gave a small amount of an unidentified oil. No crystals were obtained by trituration or scratching.

b) With Phenylacetylene in the absence of air and light

The thione (1.0g, 0.0062 mol) and phenylacetylene (1.3g, 0.0125 mol) were heated under reflux in deoxygenated, purified, chlorobenzene (30 ml) in an atmosphere of nitrogen. The experiment was carried out in a dark room, the apparatus being protected by aluminium foil to exclude light from a photographic "safe-light", and monitored by t.l.c.



After 3 h t.l.c. began to show a pink spot (r.f. = 0.6) in addition to the starting material spots. This spot increased in intensity and the yellow thione spot decreased in intensity during the reaction until, after 28 h, the yellow thione spot had practically disappeared. The reaction mixture was then concentrated and chromatographed on activated alumina, eluting with light petroleum b.p. 40-60°C-benzene to give the following fractions:-

- 1) a yellow band which produced a very small amount of oil (<0.01g) which was not identified.
- 2) a red band which afforded red crystals. Recrystallisation from ethanol gave red needles (0.58g), m.p. 149-150° which were shown to be identical (mixed m.p. infra-red spectrum) with the trithiapentalene obtained in the presence of air and light.
- 3) a yellow band which yielded the original thione (0.18g)
- 4) a yellow band which gave an unidentified oil (<0.01g).

c) With Phenylpropionic acid

The thione (0.50g, 0.003 mol), phenylpropionic acid (0.45g, 0.003 mol) and methylene dichloride (30 ml) were heated under reflux and the reaction was monitored by t.l.c. (silica-benzene). After 2 h, a brown spot (r.f. 0.05) began to appear in addition to the starting materials and this increased in intensity as samples were taken until, after 26 h, a pink spot (r.f. = 0.60) began to appear. This pink spot suggested the formation of the thiathiophthen and so heating was discontinued.

The solvent was removed, benzene was added, and the solution was heated under reflux for 3 h in order to decarboxylate the adduct which had presumably been formed.

The benzene was removed in vacuo and the residue was chromatographed on alumina (10% deactivated) eluting with light petroleum b.p. 40-60°C to give the following fractions:-

1) a pink band which yielded crystals (0.05g). The i.r. spectrum was identical with that of 2,3-dimethyl-5-phenyl-1,6,6a-trithiapentalene.

2) a brown band which yielded a reddish-brown solid (0.10g) m.p. 107-108°, the i.r. spectrum of which contained no peaks in the 1600 cm<sup>-1</sup> → 1800 cm<sup>-1</sup> region. This is probably a mixture of the original thione and the adduct, 2-thioacylmethylene-1,3-dithiole but further chromatographic separation could not be achieved.

Mass Spectrum:  $m/e$  (% abundance): 264 (P, 50%); 249 (3%); 231 (5%); 210 (5%); 196 (5%); 162 (100%).

3) a yellow band which yielded a yellow oil (0.10g) which could not be crystallised.

The experiment was repeated using "Analar" benzene as solvent, and the same quantities of reactants. The colour of the reaction mixture changed from yellow to maroon after 30 minutes, and t.l.c. showed a dark spot near the baseline. Heating was continued and, after 20 h, a pink spot had appeared (r.f. = 0.60). The heating was discontinued and the solution concentrated. Chromatography on alumina (10% deactivated) and eluting with light petroleum b.p. 40-60°C-benzene mixtures, gave:

1) a faint yellow band which gave no identifiable product.

2) a pink band which gave a red oil. Trituration with benzene-ethanol and recrystallisation from ethanol gave a red solid (0.26g), m.p. 148-149°C, (mixed m.p. with the trithiapentalene (148-149°C)).

3) an orange band which gave the original thione (0.17g).

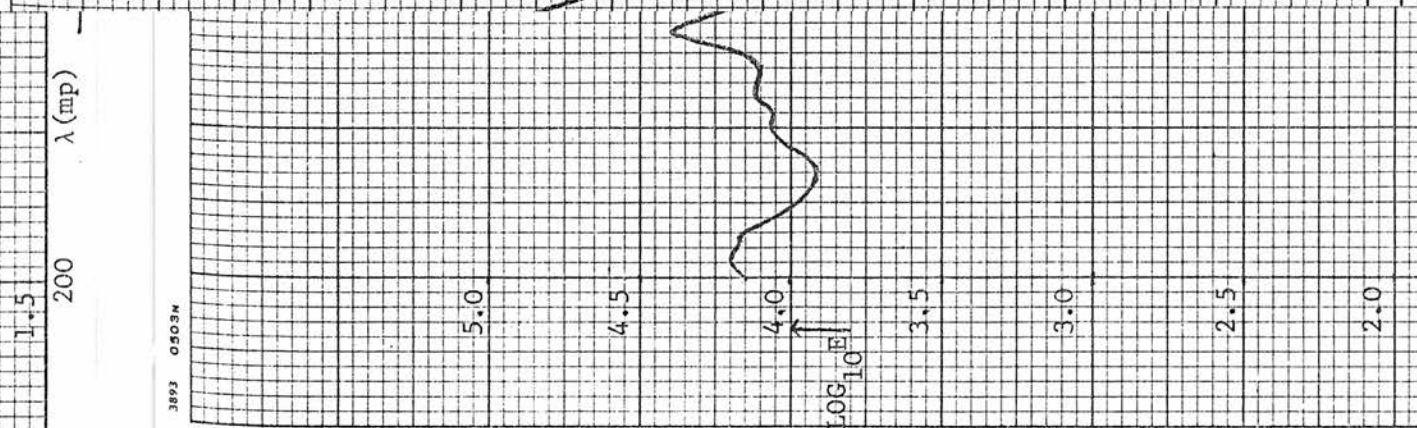
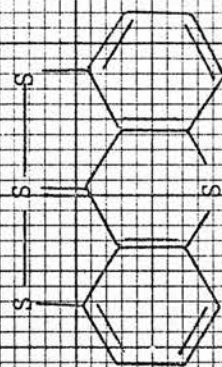
4) an orange band which yielded a dark red solid

recrystallising from methylcyclohexane as brown crystals (0.20g).

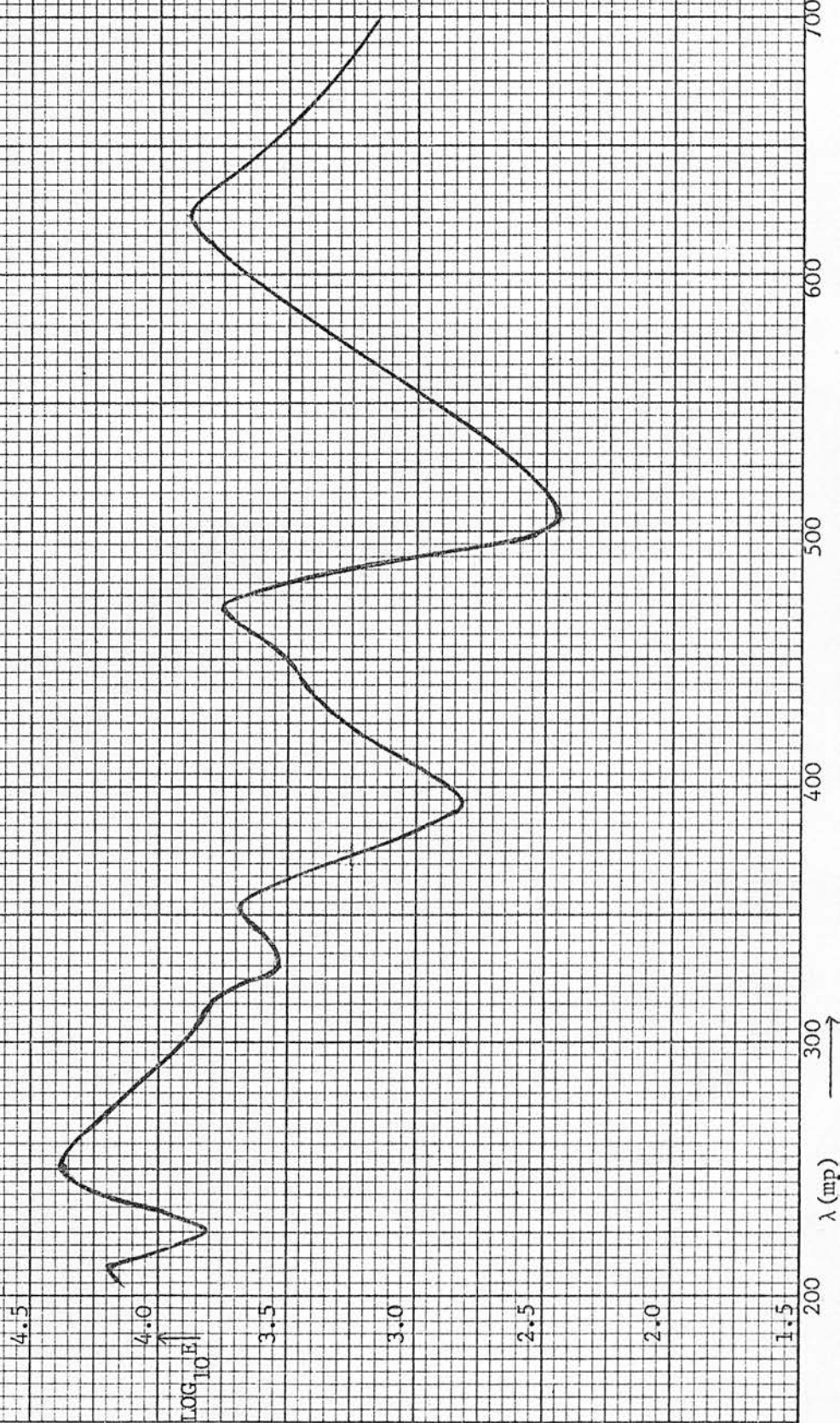
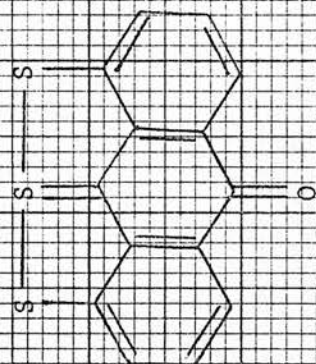
The p.m.r. spectrum showed that this was probably a mixture of the original thione and the required 2-thioacylmethylene-1,3-dithiole but further chromatographic separation could not be achieved.

Ultraviolet Spectra

binding margin; when preparing diagrams for reports, always leave a margin of two centimetres or more for binding; when using A3 paper, which is twice this size, leave the margin along the shorter side.







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